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ON THE CATALYTIC ACTION OF JAPANESE ACID EARTH. X. THE MECHANISMS OF THE PROMOTION AND POISONING OF THE CATALYTIC ACTION.*

By Koshiro ISHIMURA.

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The Mechanism of the Promotion. It has been suggested in a previous paper[1] that the co-existence of Al_2O_3 and SiO_2 is essential to the catalytic action of Japanese acid earth on naphthalene and all other metallic oxides are unnecessary for it. There has been, however, always present in the reaction system another component not to be overlooked, i.e. water. The earth heated at 500° still contains a few per cent. of water.[2] Isobe[3] observed that it retains a small amount of water even after heated at 1000° for six hours.

The earth dried at 300° rapidly adsorbs water vapour. A small fraction of this adsorbed water is held very firmly by the earth and cannot be set free at 120° even after the constant weight of the earth is obtained. This tenaciously held water has been called "retained water" by the present author[4] in order to distinguish it from adsorbed or added water. The molecules of the retained water may highly probably be those directly held by the bare surface of the earth. The catalytic activity of the earth is greatly promoted when it carries the retained water as described in details in the preceding paper. Therefore, it is very probable that the catalysis in question is performed by the three component catalyst consisting of Al_2O_3, SiO_2, and water; the molecules of naphthalene are activated when they are adsorbed on the catalytically active centres of these three components.

When the earth is heated at 300° some of these active centres lose molecules of water and consequently become inactive. They will, however, recover their ability if water molecules are put in their original positions, and this recovery of the catalytic activity is accomplished by the retained

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(1) Inoue and Ishimura, This Bulletin, **9** (1934), 431.
(2) Ishimura, This Bulletin, **9** (1934), 522.
(3) Isobe, *J. Chem. Soc. Japan*, **51** (1930), 761.
(4) Ishimura, *loc. cit.*

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water, giving rise to the observed promotion of the activity. The promotion would be therefore necessarily accompanied by the increase in the water content of the earth. On the contrary, if the promotion is caused by the increase in the surface area due to the prolonged exposure to water vapour in the same manner as many metals are activated by the adsorption of gases,[5] the promotive power would be a function of the time of adsorption or of the total amount of adsorbed water but not of the amount of retained water. The experimental results however contradict with the latter view. When water is adsorbed in the absence of air the adsorption proceeds much more rapidly and the ratios of retained water to the total amounts adsorbed are much greater than in the case of the adsorption in the open air. By comparing the promotive powers of the samples thus prepared with those given in Table 2 in Part IX of this series,[6] one comes at once to the conclusion that the promotive power is a function of the amount of retained water but not of the total amount adsorbed nor of the time of adsorption. Moreover, when the moist earth is dried at 120° under highly reduced pressure the amount of the retained water is diminished with the decrease in the promotive power.

Thus it is most probable that the existence of water is indispensable for the promotion of the catalytic activity.[7]

As always stated,[8] the retained water can be replaced by other neutral substances containing oxygen in their molecules such as alcohols, acetone, and ether. So, generally speaking, the catalytic action on naphthalene is effected by the three component catalyst consisting of Al_2O_3, SiO_2, and one of these substances mentioned above.

The Mechanism of the Poisoning. The poisons in this catalytic action can be classified into two distinct types: strong poisons such as ammonia, amine, nitrile, and amyl nitrite, and weak poisons such as hydrogen chloride and acetic acid. The mechanism of poisoning will be discussed separately about each type.

Though poisoning by ammonia is very drastic, its action is not fatal to the active centres. The catalytic activity will be restored completely if the adsorbed poison is all expelled. It is very difficult however to liberate the total ammonia retained. The complete liberation was attained only when

(5) It is believed that molecules of gas diffusing through metal actually enter into metal lattice, distending it, breaking it, and thus activating the surface of the metal. Piper, *Trans. Faraday Soc.*, **24** (1933), 540.

(6) Ishimura, This Bulletin, **9** (1934), 523.

(7) It goes without saying that the promotion is not a mere annealing effect.

(8) Ishimura, *loc. cit.*

the poisoned earth was heated at 500° for two hours under the reduced pressure of 4 mm. The activity of the earth thus freed from the retained ammonia was compared with that of the original sample with the same heat treatment and there could be seen no difference between them.

The earth with the sufficient amount of the poison to cover the whole surface does not recover its activity by adsorbing water or alcohol. When, however, its surface is only partly covered by the poison and there is left an ample room to retain these oxygen-containing neutral substances, then the activity is increased to a marked degree by the adsorption of these substances. It seems therefore that the strong poisons are adsorbed selectively and strongly on the active centres, rendering them inactive for the catalysis.

This is not the case with the weak poisons such as hydrogen chloride and acetic acid. Though they are in themselves poisons their selection of the location of adsorption would be different; they are adsorbed first and retained to the very last on the inactive parts of the surface. Their poisoning effects are not therefore manifested unless their retained amounts are relatively large, and even if all the active centres are covered by them they may be liberated easily in the course of reaction, hence the weakness of their poisoning actions.

The amount of naphthalene adsorbed by the acid earth with the various retained substances are plotted against time as shown in Fig. 1.

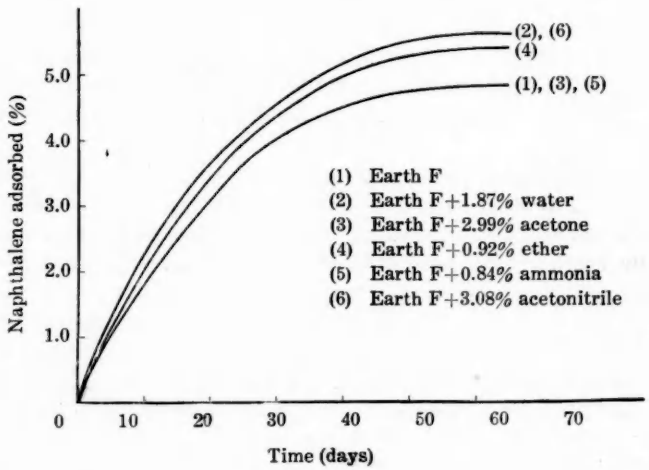

Fig. 1.

The adsorption experiment was carried out in the same manner as described in the previous paper.[9] Fig. 1 shows that the total amount adsorbed is not influenced appreciably by the retained substance, whether it is a promoter or a poison. Therefore the rôle of poisons does not consist in the prevention of the adsorption of naphthalene. They only render the catalytically active parts inactive before there occurs the adsorption of naphthalene. In other words, the adsorption of naphthalene is converted from the "chemical" into the "physical" by the poisons.

The Surface Area of the Acid Earth. The surface area per gram of the acid earth was calculated from the specific gravity and diameter of the particles of the earth. Kobayashi[10] measured the specific gravities of the dried earths and gave the values 2.7—2.9, while Isobe[11] 2.67—2.70. Recently Yamamoto[12] determined them again and found 2.4~2.5. The value 2.7 was taken in the present calculation. The diameter of the particles of the dried earth is presumed to be less than 10^{-5} cm. from the observation of X-ray patterns.[13] Isobe[14] determined it from the apparent and true specific gravities and the number of cracks on the surface of the earth observed by a microscope and found the value 2.35×10^{-5} cm., while Kobayashi[15] gave $3.3\sim6.2\times10^{-5}$ cm. by counting the number of particles suspended in water using an ultramicroscope and measuring the weight after evaporating up the water. The value 2×10^{-5} cm. was here adopted.

Let us assume that each particle is cubic in form with the sides of 2×10^{-5} cm. in length, then the surface area of one particle is 2.4×10^{-9} sq. cm. Since the specific gravity is 2.7, the number of particles contained in 2.7 g. is $(1/2^3)\times10^{15}=1.25\times10^{14}$, hence the number of particles per gram is 4.63×10^{13}. The total surface area per gram is therefore 1.11×10^{5} sq. cm. $\fallingdotseq$ 10 sq. m. This represents about one tenth of the surface area[16] of active charcoal.

As stated in the previous paper, when 0.49 millimol of ammonia is retained by one gram earth, the activity of the earth is entirely lost. Further experiment showed that by 0.15 millimol of ammonia retained by one gram earth the activity was decreased by 77 per cent. Adopting a

(9) Ishimura, This Bulletin, **9** (1934), 498.
(10) Kobayashi, "Japanese acid earth," 2nd Ed. (1927).
(11) Isobe, *Sci. Pap. Inst. Phys. Chem. Research (Japan)*, **5** (1926), 175.
(12) Yamamoto, *Waseda Appl. Chem. Soc. Bull.*, No. **17** (1932), 2.
(13) Kameyama and Oka, *J. Soc. Chem. Ind. Japan*, **33** (1930), 307.
(14) *Loc. cit.*
(15) *Loc. cit.*
(16) Cude and Hullet, *J. Am. Chem. Soc.*, **42** (1920), 398; Lamb and Coolidge, *ibid.*, **42** (1920), 1168.

value of 6.06×10^{23} for the Avogadro constant and 1.6×10^{-8} cm. for a molecular diameter of ammonia, we obtain an area of 1.71×10^{4} sq. cm. to be covered by 0.15 millimol of ammonia on the assumption of a packed monomolecular layer. Therefore, the total area of the active centres per gram earth is 2.22×10^{4} sq. cm. or about 20 per cent. of the total surface area. This represents the greatest value possible, since the adsorption of ammonia is not necessarily quite selective and moreover the liberation of ammonia from the active centres may occur in the course of the reaction.

A simple calculation shows that the amount of water to cover the whole surface of the earth by a monomolecular layer would be about 2.5 per cent. of the weight of the dry earth, if the effective diameter of water molecule on the adsorption layer is 3.5×10^{-8} cm.(17)

The author expresses his sincere gratitude to Dr. Inoue for his interest taken in and criticism made on this work.

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ON THE ABSORPTION OF HYDROGEN CHLORIDE INTO VARIOUS ORGANIC LIQUIDS AND CALCULATION OF THE HEAT OF ABSORPTION. I.

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On account of the great interest in solubility in general, and especially in the possible relations between various physical and chemical properties of solutes as well as of solvents and solubilities, numerous investigations have been carried out. However, there is not yet a theory which enables us to account for all types of solubility (dada,) although there is a definite trend

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(17) This is not known accurately and must depend upon the orientation of molecules. It may be less than the above-mentioned value since it is probable that molecules on the adsorption layer are more closely packed than in liquid state.

as to what direction we should look for. Hildebrand gives an excellent discussion in his book "Solubility" and he states in his introductory remark, "The solubility of one substance in another depends fundamentally upon the ease with which the two molecular species are able to mix, and if the two species display a certain hostility towards mixing, not only will saturation be attained at smaller concentration, but in the unsaturated solution the tendency to mutual segregation will give rise to a partial separation or adsorption of one species at the surface, with a consequent lowering of surface tension. It is likely also to give rise to an expansion and absorption of heat upon mixing, phenomena not ordinarily connected with solubility". Thus the investigation of solubility is not only highly practical, but also very fascinating and interesting from a theoretical standpoint. With this view, the present author has undertaken the investigation on some aspects of solubility of gases in various organic solvents.

In order to systematize various solubility data several attempts have hitherto been done to find general laws which govern the solubility. We have a great deal of evidences that polarity of substances involved has much to do with the solubility. Still another criterion which has been taken into account is the relations between the solubilities and the internal pressures of substances, as measured by $-T\frac{\alpha}{\beta}$ which was proposed by Dupré :[1][2]

$$T\left(\frac{\partial P}{\partial T}\right)_V = -T\frac{\alpha}{\beta}\,, \tag{1}$$

where α is the coefficient of expansion, β the coefficient of compressibility, and the term $T\left(\frac{\partial P}{\partial T}\right)_V$ appears in the thermodynamic equation of state, namely

$$P+\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V . \tag{2}$$

The purpose of the present investigation is to see whether the solubility of a relatively polar gas in various non-polar liquids can be correlated with the various chemical and physical properties of these non-polar liquids.

(1) Dupré, *Ann. chim. phys.*, **2** (1864), 201.

(2) For fuller discussion of internal pressure, see "Solubility" by Hildebrand, Chem. Catalogue Co.

As a polar gas hydrogen chloride[2a][3] is chosen, and as non-polar liquids carbon tetrachloride, ethylene chloride, ethylene bromide, and 1,1,2,2-tetrachlorethane are selected.

Experimental Procedure. The method for measuring the absorption of hydrogen chloride into these liquids consists in finding the volume of hydrogen chloride absorbed by a given amount of these liquids. The measuring apparatus of hydrogen chloride is a U-shaped gas burette which is filled with mercury, and calibrated to 0.5 c.c., and can be read to 0.1 c.c., and at the same time the pressure of hydrogen chloride plus the vapour pressure of the liquid used, which has absorbed hydrogen chloride also can be read so that the amount of hydrogen chloride absorbed at various pressures can be obtained. The U-shaped gas burette is provided with water jacket. During a run there is practically no variation of temperature, so that the water in the jacket is stopped from flowing. The absorption vessel is about 80 c.c. in capacity and connected to the gas generating system through a capillary tube and also to an ordinary mercury manometer with a stopcock to cut it off from the absorption chamber during the absorption experiment. The vessel is also connected to the graduated liquid reservoir at the top from which a given amount of liquid is introduced into the absorption vessel after the vessel has been evacuated. The whole absorption vessel is immersed in the thermostat with constancy of $\pm 0.1°$. Between the gas burette and the absorption chamber a vessel of 335 c.c. capacity is inserted as a gas reservoir which is also immersed into the thermostat in order to make the gas to acquire the same temperature as the liquid before entering the absorption vessel. Furthermore, in order to saturate the liquid with hydrogen chloride thoroughly, the whole absorption apparatus is shaken by tapping from time to time until there occurs no more absorption. One to one and a half hours are usually sufficient to establish the equilibrium. Thus from the volume change in

(2a) Debye, "Polar Molecules," Chem. Catalogue Co.; F. I. G. Raulins, *Z. Physik*, **50** (1928), 440; J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford Press; L. Pauling, *J. Am. Chem. Soc.*, **54** (1932), 988.

(2b) L. Pauling, "The Nature of The Chemical Bond. IV," *J. Am. Chem. Soc.*, **54** (1932), 3570.

(2c) L. Pauling and J. Sherman, *J. Chem. Phys.*, **1** (1933), 606.

(3) Recent development in the quantum mechanics seems to show that as far as the valence in HCl is concerned it may be regarded perhaps more non-polar in nature, although it is more or less accepted as a polar gas from the dielectric measurement and the direct measurement of the electric moment by the molecular ray method. Zahn, *Phys. Rev.*, **24** (1924), 400; Estermann and Fraser, *J. Chem. Phys.*, **1** (1933), 390.

the gas burette, the initial and final pressures, and the volume of the system, the volume (ΔV) of hydrogen chloride actually absorbed into the liquid is calculated.

The Materials Used. Hydrogen chloride was prepared by dropping concentrated hydrochloric acid into pure concentrated sulphuric acid, passing the gas through two sulphuric acid bubblers, and condensing twice with liquid nitrogen. Only the middle portion of it was used after passing it finally through a calcium chloride tube before it was allowed to enter into the burette and reservoir.

1,1,2,2-Tetrachlorethane (Kahlbaum's product, b.p. 143.5—144°) was distilled twice. The another sample of 1,1,2,2-tetrachlorethane was kindly supplied by Dr. Fukagawa of the Institute of Physical and Chemical Research, Tokyo, to whom the author wishes to express his best thanks.

Carbon tetrachloride (Kahlbaum's product, b.p. 76.0°), ethylene chloride (Takeda's product, b.p. 83.0°), and ethylene bromide (Takeda's product, b.p. 129.0°) were all distilled twice.

Results. For all of these organic liquids, the volume of hydrogen chloride absorbed was plotted against respective pressures at which the system finally reached an equilibrium, one of examples, of 1,1,2,2-tetrachlorethane being shown in Fig. 1, so that we can get the volume of the gas to be absorbed at the total pressure of 760 mm. by either extrapolation or interpolation as the case may be, and this is converted to mol fraction: $N'_{HCl} = n_{HCl}/(n_{HCl}+n_{liquid})$. This corresponds to the solubility of hydrogen chloride at the total pressure of 1 atmosphere expressed in mol fraction. To find the value of the solubility of hydrogen chloride, i.e. N_{HCl}, when P_{HCl} equals 1 atmosphere, Henry's law in the following form was used:

$$N_{HCl} = N'_{HCl} \times \frac{760}{P_{HCl}} .$$

In order to find P_{HCl}, Raoult's law was assumed to hold and the values of the vapour pressures of the organic liquids were obtained from the International Critical Table and those not given directly was calculated by the equation:

$$\log_{10} P_{mm.} = \frac{0.05223}{T} \times A + B . \qquad (4)$$

In the case of 1,1,2,2-tetrachlorethane the data for the above expression could be obtained only for the range 26—145°, so that strictly speaking the

vapour pressure calculation could not be correct, but, for the temperatures 15°, 20°, and 25°, calculation may not be so much far from the true values even if we assume it holds for 15°, 20°, and 25°C.

Tables 1–4 show the results of the absorption experiments for 20 c.c. of respective liquids at 15°, 20°, and 25°C. In Table 5, N, $\log N$, and $\frac{1}{T}\times 10^{-3}$ for 15°, 20°, and 25° for each liquid are listed, and $\log N$ plotted against $\frac{1}{T}\times 10^{-3}$ as shown in Figs. 2–4. The heat of absorption ΔH can be calculated by

$$\frac{d\log N}{d\left(\frac{1}{T}\right)} = \frac{-\Delta H}{2.303\times R}\,. \qquad (5)$$

ΔH for each liquid is also listed in Table 5.

Table 1. Absorption of Hydrogen Chloride into 1,1,2,2-Tetrachlorethane at 25°, 20°, and 15°C., per 20.0 c.c. of $C_2H_2Cl_4$.

Exp. No.	Pressure P mm.	Vol. of absorbed HCl reduced to $V_{25°}$ c.c.	Mol fraction N	Mol per cent.
		25°C.		
1	739.0	112.55	0.0239	2.39
2	396.0	59.38	0.0128	1.28
3	493.5	74.90	0.0161	1.61
4	614.5	94.18	0.0201	2.01
5	541.0	83.41	0.0178	1.78
6	442.0	68.04	0 0146	1.46
		20°C.		
7	731.5	122.05	0.0258	2.58
8	390.0	65.29	0.0140	1.40
9	582.0	99.27	0.0211	2.11
10	631.5	108.21	0.0229	2.29
11	680.0	114.97	0.0243	2.43
12	621.5	106.25	0.0225	2.25
		15°C.		
13	663.5	124.30	0.0261	2.61
14	384.5	72.81	0.0155	1.55
15	722.5	133.84	0.0281	2.81
16	573.5	109.81	0.0231	2.31

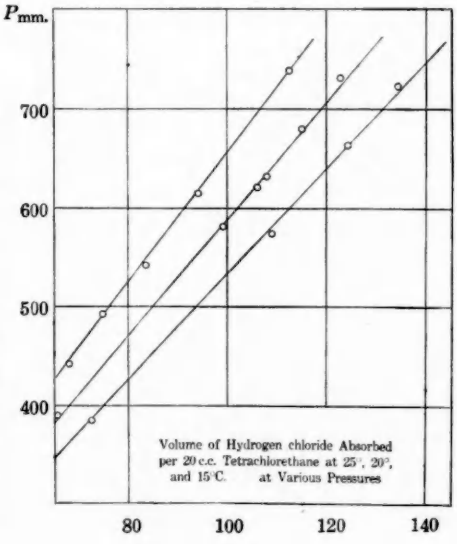


Fig. 1.

Table 2. Absorption of Hydrogen Chloride into Carbon Tetrachloride at 25°, 20°, and 15°C., per 20.0 c.c. of CCl_4.

Exp. No.	Pressure P mm.	Vol. of absorbed HCl reduced to $V_{25°}$ c.c.	Mol fraction N	Mol per cent.
		25°C.		
1	631.5	40.90	0.00817	0.817
2	779.5	60.42	0.01200	1.200
3	433.5	18.28	0.00367	0.367
4	531.5	31.09	0.00622	0.622
5	680.5	47.89	0.00955	0.955
6	580.0	37.86	0.00757	0.757
		20°C.		
7	770.5	70.25	0.01380	1.380
8	425.0	28.33	0.00563	0.563
9	521.0	41.83	0.00829	0.829
10	572.0	44.22	0.00876	0.876
		15°C.		
11	614.0	59.89	0.01170	1.170
12	420.5	31.10	0.00613	0.613
13	515.5	47.24	0.00928	0.928
14	664.0	64.99	0.01270	1.270

Table 3. Absorption of Hydrogen Chloride into Ethylene Chloride at 25°, 20°, and 15°C., per 20.0 c.c. $C_2H_4Cl_2$.

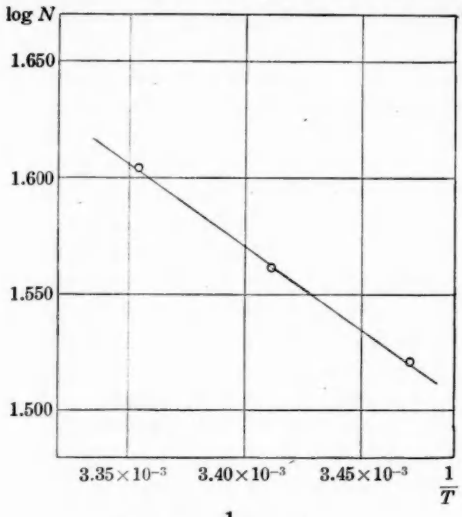
Exp. No.	Pressure P mm.	Vol. of absorbed HCl reduced to $V_{25°}$ c.c.	Mol fraction N	Mol per cent.
		25°C.		
1	680.0	183.09	0.0291	2.91
2	467.5	123.49	0.0198	1.98
3	500.0	133.20	0.0213	2.13
4	584.0	158.00	0.0252	2.52
		20°C.		
5	526.5	163.19	0.0258	2.58
6	526.5	163.19	0.0258	2.58
7	540.0	164.64	0.0261	2.61
8	600.0	192.45	0.0303	3.03
9	731.5	223.49	0.0350	3.50
10	520.5	159.48	0.0253	2.53
		15°C.		
11	533.5	189.89	0.0298	2.98
12	342.5	118.80	0.0188	1.88
13	550.0	191.22	0.0300	3.00
14	422.0	145.20	0.0229	2.29

Table 4. Absorption of Hydrogen Chloride into Ethylene Bromide at 25°, 20°, and 15°C., per 20.0 c.c. $C_2H_4Br_2$.

Exp. No.	Pressure P mm.	Vol. of absorbed HCl reduced to $V_{25°}$ c.c.	Mol fraction N	Mol per cent.
		25°C.		
1	672.0	155.08	0.0269	2.69
2	507.0	117.81	0.0206	2.06
3	368.5	87.16	0.0153	1.53
4	601.0	138.96	0.0242	2.42
5	279.0	66.40	0.0117	1.17
		20°C.		
6	362.0	94.28	0.0165	1.65
7	453.5	119.11	0.0207	2.07
8	679.5	179.78	0.0309	3.09
9	496.0	129.53	0.0225	2.25
		15°C.		
10	672.0	189.96	0.0325	3.25
11	354.0	103.72	0.0180	1.80
12	531.0	154.62	0.0263	2.66
13	719.0	204.37	0.0348	3.48

Table 5.

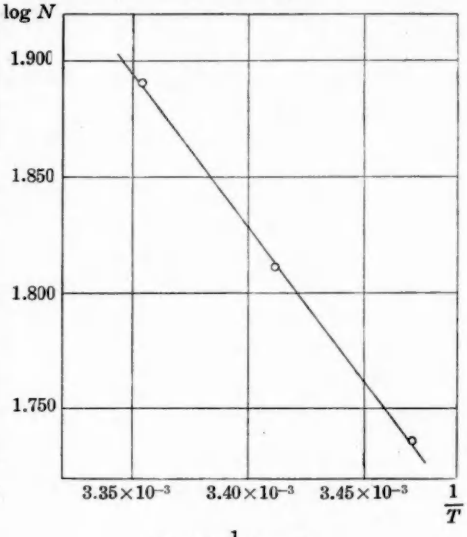
Substance	N(HCl)	log N	$1/T\times10^3$
	15°C.		
$C_2H_2Cl_4$	0.03006	1.52201	3.471
CCl_4	0.01826	1.73850	3.471
$C_2H_4Cl_2$	0.04377	1.35882	3.471
$C_2H_4Br_2$	0.03754	1.42551	3.471
	20°C.		
$C_2H_2Cl_4$	0.02744	1.56162	3.411
CCl_4	0.01550	1.80967	3.411
$C_2H_4Cl_2$	0.03993	1.39870	3.411
$C_2H_4Br_2$	0.03441	1.46332	3.411
	25°C.		
$C_2H_2Cl_4$	0.02481	1.60537	3.354
CCl_4	0.01277	1.89381	3.354
$C_2H_4Cl_2$	0.03576	1.44660	3.354
$C_2H_4Br_2$	0.03116	1.50640	3.354
Heat of Absorption, ΔH/mol in cal.			
$C_2H_2Cl_4$	3300		
CCl_4	6100		
$C_2H_4Cl_2$	3500		
$C_2H_4Br_2$	3200		



(log $N-\frac{1}{T}$ Curve)

Variation of the Absorption of Hydrogen Chloride in Tetrachlorethane with Respect to Temperature.

Fig. 2.



(log $N-\frac{1}{T}$ Curve)

Variation of the Absorption of Hydrogen Chloride in Carbon Tetrachloride with Respect to Temperature.

Fig. 3.

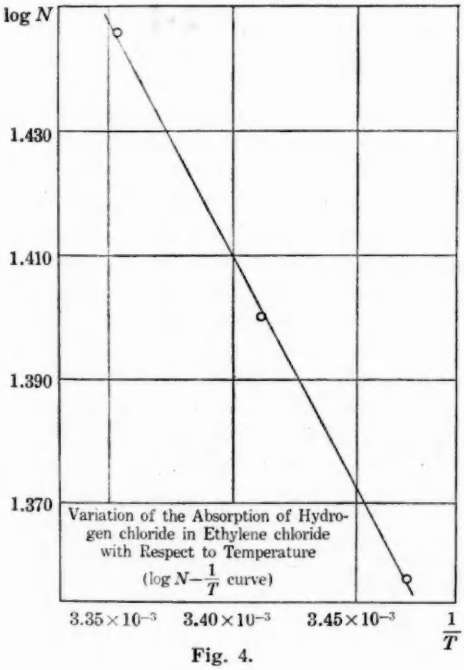
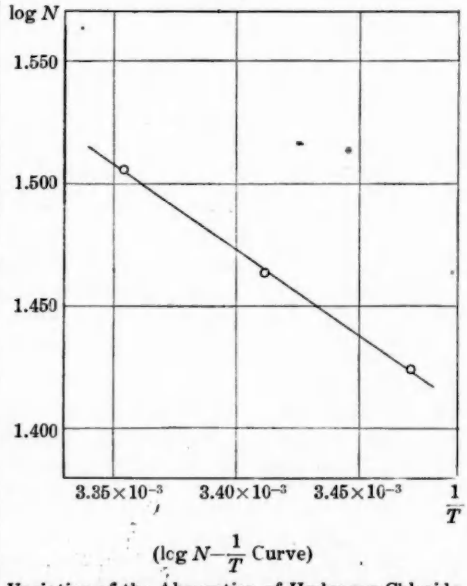


Fig. 4.



(log $N-\frac{1}{T}$ Curve)

Variation of the Absorption of Hydrogen Chloride in Ethylene Bromide with Respect to Temperature.

Fig. 5.

Discussion of Results. (a) **Polarity in Connection with Solubility.** Whether certain liquids into which a gas is absorbed are polar or non-polar, is very significant to the determination of the solubility of that gas. There are quite convincing evidences for the effects of polarity on solubility. Usually polar gases are more soluble in polar liquids than in non-polar liquids, and non-polar gases more soluble in non-polar liquids than in polar liquids. In other words, the degree of polarity plays a very important rôle. The dielectric constant usually can be regarded as the most direct evidence of polarity and the magnitude of it may be quite conveniently considered as a measure of degree of polarity. According to Van Vleck,[2a] "A molecule may be defined as polar if it has a permanent electrical moment, i.e. an electrical moment which is on the time average different from zero even in the absence of external fields. A molecule without such a permanent moment is termed non-polar". Then polarity of a substance can be estimated from the electric moment of the molecule in question. Besides these, other factors in the molecule such as chemical structure play important parts, that is to say, polarity is influenced by certain groups or radicals such as $-NH_2$, $-OH$, $-NO_2$, $=CO$, etc. These groups substituted in the molecule usually contribute much to the polarity of the substance in question, and the symmetry in the molecule seems to play a very significant rôle in almost every possible case such as the degree of the polarity as we find in the case of CCl_4, $CHCl_3$, CH_2Cl_2, CH_3Cl, $C_2H_4Cl_2$, $C_2H_2Cl_4$, etc., among which CCl_4 is considered to be the most symmetrical and hence the least polar.

Distinction between the polarity of the substances and that of the bond should be carefully noted especially in connection with solubility. The atomic volume is also considered to be an effective factor for determining the polarity, those elements having higher atomic volumes give higher polarity, and the element having the smallest atomic volume of all known elements—carbon—gives the least polar compounds. There are still some other factors which contribute much to the determination of polarity.[4] Besides, the polar character of a substance is also dependent on the so-called polar environment, as G. N. Lewis says, "ranging from the extremely polar to the extremely non-polar.....Great as the difference is between the typical polar and non-polar substance we may show how a single molecule may, according to its environment, pass from th extreme polar to the extreme non-polar form not per saltum, but by im-

(4) For fuller discussion on polarity, see the following: Debye, "Polar Molecules"; G. N. Lewis, "Valence and the Structure of Atoms and Molecules"*; *J. Am. Chem. Soc.*, **35** (1913), 1448; *J. Am. Chem. Soc.*, **38** (1916), 762*; J. H. Hildebrand, "Solubility"; Van Vleck, "The Theory of Electric and Magnetic Susceptibilities".

perceptible gradations, as soon as we admit that an electron may be the common property of two atomic shells."[4] At any rate, the dielectric constant does give a rough measure of the polarity of the molecule with some exceptions. Therefore, it has been attempted to see any possible correlation between the solubility of hydrogen chloride in the mentioned organic solvents, and the polarity as measured by the dielectric constant, molecular symmetry, electric moment, Eötvös's constant, and the polarity with the effects of substituents. These are tabulated in Table 6. The results indicate that the solubility is in the order of increasing values of dielectric constants in the series of chlorine derivatives of hydrocarbon, i.e. hydrogen chloride being the most soluble in ethylene chloride with the highest dielectric constant 10.8 at 20°, next in tetrachlorethane with 8.2, and the least in carbon tetrachloride with 2.24; the same could be said with regards to the electric moment. In these cases, however, ethylene bromide does not seem to be accounted in the same categories. With respect to Eötvös's constants, and the molar volumes of the solvents we can hardly find any regularity.

Table 6.

Substance	D.C. 20°	$\mu\times10^{18}$	Mol. vol. c.c.	Eötvös's const.		Solubility (20°) mol fraction
				Calc.	Obs.	
1,1,2,2-Tetrachlorethane	8.2	1.6	105.30	2.26	—	0.02744
Carbon tetrachloride	2.24	0	97.10	2.20	2.10	0.01550
Ethylene chloride	10.8	1.8	78.90	2.15	—	0.03993
Ethylene bromide	6.3	1.4	86.20	2.19	2.17	0.03441
Hydrogen chloride		1.03				

Table 7.

$\mu\times10^{18}$ HCl	Solvent	Authors
1.286, 1.273, 1.32 } 1.3	Benzene, CCl_4, Cyclohexane	F. Fairbrother[5a]
1.02	Ethylene bromide	F. Fairbrother[5a]
0.97	Ethylene chloride	
1.26	Benzene	
1.034	Gaseous[5b]	Zahn
1.18	,,	Braunmühl
1.48	,,	Frivold and Hassel
2.15	,,	Falkenhangen

The electric moment of hydrogen chloride in various non-polar solvents has been reported by Fred Fairbrother.[5a] (Table 7)

Change in the effective electric moment of hydrogen chloride was found not influenced by solvents. From these we can say that, when the solvent molecules are as

(5a) F. Fairbrother, *J. Chem. Soc.*, **1932**, 43; *ibid.*, **1933**, 1541; Hassel and Uhl, *Z. physik. Chem.*, [B], **8** (1930), 187.

(5b) Zahn, *Phys. Rev.*, **24** (1924), 400; H. J. Braunmühl, *Physik. Z.*, **28** (1927), 141; O. E. Frivold and O. Hassel, *ibid.*, **24** (1923), 82; H. Falkenhangen, *ibid.*, **23** (1922), 87.

polar as those of the solute or more polar as in the solution of ethylene bromide and ethylene chloride, the electric moment is much lessened; this can be accounted parallel with the approximate proportionality of the frequency shift with the electric moment of the molecules of the solvent in "Raman spectra of hydrogen chloride in non-ionizing solvents" which was recently reported by W. West and P. Arthor.[6] This in turn means, as they remarked, that a large part of the shift is due to dipole interaction between solvent and solute molecules. The existence of dipole interaction may indicate that hydrogen chloride has greater solubility in ethylene chloride than in any other and the solubility is roughly in the order of magnitude of the electric moment of the solvents; possibly it means more dipole interaction in ethylene chloride than in others, which in turn increases the solubility, and the fact that the electric moment of hydrogen chloride increases in such solvents as CCl_4 and benzene as given by Fairbrother is true and the account that it is due to the stretching of the molecule in solution is concordant with the fact that hydrogen chloride is less soluble in CCl_4 than in $C_2H_4Cl_2$ and $C_2H_2Cl_4$.

(b) **Internal Pressure in Connection with the Solubility.** Although there is controversy as to whether the internal pressure as measured in various different ways gives some correlation with solubility or not, it is very interesting to see the actual cases. Those data selected and given in "Solubility" by Hildebrand seem to give a very good criterion in the discussion of solubility, but W. Kunerth[7] has given some contradictory evidences to usefulness of the internal pressure from the study of the solubility of CO and N_2O in some twelve organic liquids. Before we go into the detailed discussion of our results in the light of the internal pressure it would be profitable to state what we mean by the internal pressure of the liquid. Accepting a definition given by Hildebrand internal pressure is the maximum negative pressure that a liquid could support if no nuclei of vapour were allowed to form. The internal pressure can be best estimated if the internal forces which operate in liquid could be known well. We therefore, must have definite knowledge, of their equation of state for liquid in question as already stated, and of $-T\frac{\alpha}{\beta}$ as a measure of internal pressure. Relative internal pressure could be estimated in various ways, for instances, from van der Waals's equation, coefficient of expansion, heat of vaporization, boiling points $\frac{5200+30t_b}{V}$, surface tension, and total surface energy.

(6) W. West and P. Arthor, *J. Chem. Phys.*, **2** (1934), 215.
(7) W. Kunerth, *Phys. Rev.*, **19** (1922), 512.

The values of the internal pressure are not quite concordant as the methods of calculation differ and it is very difficult to find what method we should most rely upon in correlation with solubility. Some of these values of the relative internal pressure from various methods are tabulated with our solubility data in Table 8. As far as the comparison in the table is concerned, we hesitate to draw any definite conclusion upon this point.

Table 8.

Subst.	$T\frac{\alpha}{\beta}$	Mathews[6]	Sutherland[9]	$E/V^{\frac{1}{3}}$[9]	$\frac{(n-1)L}{V}$	$(5200+30t_b)/V$	Van Laar's a	$\gamma/V^{\frac{1}{3}}$	$N(20^\circ)$
CCl_4	3362[8] / 3690	2660	490	14.3	308	77.06	496	5.78	0.01550
$C_2H_4Br_2$	4455[8] / 4760	3900	710	17.2	422	105.23	549	8.7	0.03441
$C_2H_4Cl_2$	4153[8]	—	—	17.0	406	97.45	475	7.5	0.03993
$C_2H_2Cl_4$	—	—	—	15.58	368	90.72	555	7.71	0.02744

Table 9.

Bond	Bond energy in v.e.[2b][2c]
C — Cl	3.22[10]
C — Br	2.89[10]
C — H	4.34
C — C	3.6
Substance	**Total bond energy in v.e.[11]**
CCl_4	12.88
$C_2H_4Br_2$	26.74
$C_2H_4Cl_2$	27.40
$C_2H_2Cl_4$	25.16

With exception of $C_2H_4Br_2$, the solubilities of hydrogen chloride in these liquids lie in the order of their relative internal pressures.

After taking the polarity and the internal pressure into consideration of influencing factors of the solubility of hydrogen chloride gas in each case, we find that $C_2H_4Br_2$ comes out to be exceptional in these discussions, hence we must look for some additional causes. Not only the dielectric constant for determining the polarity of molecule, but also other properties of it should

(8) J. H. Hildebrand, *Phys. Rev.*, **34** (1929), 649,

(9) "Solubility" by J. H. Hildebrand.

(10) Average of values of the various authors are used:
A. Sherman and C. E. Sun, *J. Am. Chem. Soc.*, **56** (1934), 1099.

(11) "The observed energy of the molecule is equal to that calculated for an assumed distribution of bonds or differs from it in the direction corresponding to greater stability in accord with the quantum mechanical requirement that the actual energy for the normal state of any system is the lower limit for values of the energy integral calculated for any wave function". L. Pauling and J. Sherman, *J. Chem. Phys.*, **1** (1933), 607.

be taken into account. For instance, the kind of halogen substituted and chemical stability as estimated from the relative strength of bonds involved in the compound :

Total bond energy

$$C_2H_4Cl_2 > C_2H_4Br_2 > C_2H_2Cl_4 > CCl_4$$

Solubility

$$C_2H_4Cl_2 > C_2H_4Br_2 > C_2H_2Cl_4 > CCl_4$$

The solubility of hydrogen chloride lies in the order of the strength of bonds as estimated by total bond energy similarly calculated as L. Pauling has done by assuming the additivity of energy. The strength of bonds as indicated by the total bond energy can be interpreted that those with larger bond energy are more capable of standing against external disturbances such as stretching or compression of bonds in these compounds effected as the solute molecules dissolve into them; in other words, those solvents with higher bond energy are possibly more capable of holding more solute molecules.

Summary.

(1) Absorption of hydrogen chloride into CCl_4, $C_2H_4Cl_2$, $C_2H_2Cl_4$ (1,1, 2,2), and $C_2H_4Br_2$ at 15°, 20°, and 25°C. has been studied.

(2) The heats of absorption of hydrogen chloride into these solvents were calculated.

(3) The relations between the solubility and polarity of organic liquids involved, and also the internal pressure have been discussed.

(4) The solubilities of hydrogen chloride in these liquids have been found in the order of increasing bond energies of the liquids calculated similarly as Pauling has done, and a possible explanation of it has been suggested.

In conclusion, the author wishes to express the best thanks to Prof. S. Mitsukuri for his kind advices and suggestions in the course of this investigation, also thanks that a part of the expenses has been paid from the grant given to Prof. S. Mitsukuri by the Saito Gratitude Foundation.

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ÜBER DIE MULTIKONDENSATION DER FUMAR- UND MALEINSÄURE MIT ÄTHYLENGLYKOL.

Von Yojiro TSUZUKI.

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Einleitung. Über die Reaktion der Fumar- und Maleinsäure mit Äthylenglykol (in Form der Derivate) liegen einige ältere Versuche vor. Schon vor 40 Jahren hat Vorländer durch die Einwirkung von Äthylenbromid auf das Silbersalz der Fumar- und Maleinsäure neutrale Äthylenester erhalten.(1) Diese Äthylenester gaben nicht übereinstimmende Werte von Molekulargewicht, aber er hat diesen Substanzen die dimere Molekularformel $(C_6H_6O_4)_2$ zugeschrieben nach Analogie von dem gleicherweise erhaltenen Bernsteinsäure-Äthylenester. Später haben Carothers und Arvin sehr hochpolymere (vermutlich) Reaktionsprodukte erhalten, wenn sie Fumarsäure- und Maleinsäure-diäthylester mit Äthylenglykol auf hoher Temperatur erhitzten, aber sie konnten nicht ihre Molekulargewichte bestimmen, weil diese Äthylenester ganz unlöslich in allen Lösungsmitteln waren.(2) Ausserdem haben Carothers und Arvin wie auch Vorländer mehrere Zahlenwerte der Elementaranalyse angegeben, die von der Theorie merklich abwichen.

Um die Kenntnisse über die Molekulargrösse sowie über die Zusammensetzung der Kondensationsprodukte von Fumar- und Maleinsäure mit Äthylenglykol zu gewinnen, habe ich die vorliegenden, präparativen Versuche ausgeführt, dabei habe ich auch für die Reaktionsweise noch ein Interesse genommen. Nach Carothers' Grundgedanken über „Polymerisation and Ring Formation"(3) müssen immer hochmolekulare Verbindungen von Kettenstruktur resultieren (mit Ausnahme von einigen Fällen d. Ringbildung), wenn zwei zwei- oder mehrfunktionelle Molekülarten miteinander reagieren; aber es ist dabei zu denken, dass der räumliche Bau der reagierenden Moleküle auf die Molekulargrösse (Kettenlänge) der resultierenden Substanzen oder auf ihre Ausbeute beeinflussen.

Reaktion. Es ist jedoch tatsächlich aufgefunden worden, dass es ziemlich schwer ist, die Reaktion dieser beiden Säuren mit Äthylenglykol unter ganz gleichen Bedingungen miteinander zu vergleichen. Die

(1) *Ann.*, **280** (1894), 167.
(2) *J. Am. Chem. Soc.*, **51** (1929), 2560.
(3) *J. Am. Chem. Soc.*, **51** (1929), 2548.

Ursache der Schwierigkeit ist darauf zurückzuführen, dass bei niedriger Temperatur Fumarsäure infolge ihres hohen Schmelzpunktes sowie ihrer Schwerlöslichkeit ungewöhnlich reaktionsträge ist, während sich Maleinsäure unter dem Einfluss der Temperatursteigerung leicht umwandelt.

Wenn man Maleinsäure mit Äthylenglykol über 130° erhitzt, so geht sie erheblich in Fumarsäure über. Dagegen, wenn man ein äquimolares Gemisch von Fumarsäure und Äthylenglykol—ein „ideales" System für Multikondensation[4]—erhitzt, tritt die Reaktion unter 150° nur langsam ein, da Fumarsäure ganz schwer in Lösung geht. Somit wurde versucht, unter Anwendung geeigneter Lösungsmitteln, wie Cyclohexanon, Dioxan bei möglichst niedriger Temperatur Fumarsäure-Ester zu gewinnen, aber dies bewies sich erfolglos. Die niedrigste Temperatur für Fumarsäure, bei welcher die Reaktion eintritt ist 135–140°, hierbei aber nur unter Anwendung überschüssiges Äthylenglykols, welches auch dabei als Lösungmittel wirkt. Wenn man ein äquimolares Gemisch von Fumarsäure und Äthylenglykol über 150° erhitzt, tritt die Reaktion langsam ein, indem sich Fumarsäure allmählich verflüssigt. Je länger die Reaktionsdauer und je höher die Reaktionstemperatur ist, umso mehr entstehen dabei hochmolekulare Kondensationsprodukte, wie man in dem experimentellen Teile sieht. Wenn man Zinkchlorid als Katalysator anwendet, so wird die Reaktion dadurch ziemlich beschleunigt, aber bei höherer Temperatur dagegen wirkt der Katalysator depolymerisierend.

Da Maleinsäure, wie oben erwähnt, bei höherer Temperatur leicht umgewandelt wird, wurde die Reaktion mit Äthylenglykol bei möglichst niedriger Temperatur ausgeführt. Erhitzt man Maleinsäure mit äquimolarer Menge Äthylenglykol einige Stunden bei 120–126°, kann man Kondensationsprodukte (verhältnismässig niedermolekulare) gewinnen, wenn auch mit einer geringen Ausbeute. Erhitzt man dieses Gemisch bei derselben Temperatur nur eine Stunde, so entstehen nur niedermolekulare, wasserlösliche Produkte, die von der unveränderten Maleinsäure nicht getrennt werden können. Steigert man die Temperatur auf 155–160°, so kann man mit nur einstündiger Reaktionsdauer einige Menge Kondensationsprodukte erhalten, wobei aber eine beträchtliche Umwandlung der Maleinsäure stattfindet. Erhitzt man noch längere Zeit, so beobachtet man, dass etwa ein Drittel der Säurenmenge im Produkte in Fumarsäure umgelagert werden. In Gegenwart von Zinkchlorid als Katalysator wird die Reaktion schon bei niedriger Temperatur (115–120°) ziemlich beschleunigt, aber die Umwandlungsgefährlichkeit wird vermehrt; bei 1-stündiger Reaktionsdauer ist die Umlagerung nicht

(4) Dieser Ausdruck, nach W. Chalmers, *J. Am. Chem. Soc.*, **56** (1934), 922.

merkwürdig, bei 3-stündiger aber beträchtlich (2/3), und bei hoher Temperatur wie 150–160° wird die Maleinsäure nur bei 1-stündiger Reaktionsdauer grösstenteils umgewandelt. Ebenfalls wie bei Fumarsäure, schreitet der Kondensationsprozess bei Maleinsäure je noch weiter, je nach der Grösse der Reaktionsdauer und der Temperatursteigerung.

Konstitution der Reaktionsprodukte. Die Moleküle der durch diese Reaktionen entstandenen Polyester sind, wie Carothers an anderen Beispielen gezeigt hat,[5] kettenförmig aufgebaut und tragen, wie ich bei dem sauren, polymeren Glutarsäure-Äthylenester deutlich bewiesen habe,[6] eine freie Carboxylgruppe an einem Ende ihrer langen Ketten. Die Molekulargrösse, die durch Titrierung der End-Carboxylgruppe ermittelt wird, stimmt ziemlich gut mit der ebullioskopischen überein. Daraus folgt, dass alle diese saueren Ester die Struktur $HO\text{-}[OC\text{-}CH = CH\text{-}CO\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}]_n\text{-}H$ haben. Tatsächlich ist diese Schlussfolgerung auch durch die an der Verseifung der neutralisierten Ester erhaltenen Versuchsresultate bestätigt worden. Das heisst: das Verhältnis von *Neutralisationswert* zu *Verseifungswert*,[7] welches experimentell gefunden ist, stimmt ziemlich gut mit dem Verhältnis überein, welches aus der Molekulargrösse (die durch die Endgruppen-Bestimmung unter Annahme der obenerwähnten Kettenstruktur ermittelt wird) in folgender Weise berechnet wird. Zwischen diesen Quantitäten bestehen selbstverständlich die folgenden, numerischen Beziehungen:

$$M = nC_6H_6O_4 + H_2O = n \times 142 + 18\,,$$
$$\gamma_{ber.} = 2n - 1\,.$$

Hier bedeutet M Molekulargrösse, n Multikondensationsgrad, $\gamma_{ber.}$ berechnetes Verhältnis von Neutralisationswert zu Verseifungswert.

Das wirklich aufgefundene Verhältnis $\gamma_{gef.}$ bzw. Multikondensationsgrad n ist nicht eine ganze Zahl. Dies ist aber ein natürliches Ergebnis; denn beim Multikondensationsprozess geht die Reaktion schrittweise vor, wie Chalmers kürzlich über den Mechanismus theoretisch diskutiert hat.[8] Daher ist das entstandene Reaktionsprodukt immer ein

(5) W. H. Carothers und J. A. Arvin, *J. Am. Chem. Soc.*, **51** (1929), 2560; und spätere zahlreiche Mitteilungen, Literatur-Verzeichnis: F. J. van Natta, J. W. Hill, und W. H. Carothers, *J. Am. Chem. Soc.*, **56** (1934), 455.

(6) Y. Tsuzuki, Dieses Bulletin **8** (1933), 313.

(7) *Neutralisationswert* = c.c. der für die Endcarboxylgruppen-Titrierung von Einheits-Gew. Ester gebrauchten N/10-KOH Lösung. *Verseifungswert* = c.c. der für die Verseifung der soeben neutralisierten Esters gebrauchten N/10–KOH Lösung.

(8) *J. Am. Chem. Soc.*, **56** (1934), 921.

Gemisch von verschiedenen Gliedern der polymer-homologen[9] Reihe. Folglich stellt die oben geschilderte Grösse M, n bzw. $\gamma_{ber.}$ der mittlere Wert eines solchen Gemisches dar.

Es ist eine mühevolle Aufgabe, aus diesem Gemisch eine einheitliche Substanz, nämlich ein einziges Glied der polymer-homologen Reihe zu isolieren. Ich habe daher verzichtet, dieses Gemisch zu fraktionieren, sondern habe mich bemüht, die unveränderte Säure und Glykol zu entfernen, wobei sehr niedrige Glieder auch beseitigt worden sind.

Eigenschaften der Reaktionsprodukte. Über die Eigenschaften dieser Polyester wird zusammenfassend im folgenden dargelegt. Bei der Fumarsäureester reihen sich ihre Durchschnitts-Molekulargrössen zwischen 700 und 1300 an. Niedermolekulare Produkte bilden schmierige, weisse Masse, aber Hochmolekulare weisses Pulver. Sie schmelzen im allgemeinen unscharf, das Schmelzpunktsintervall ist ungefähr 2–10°. Ihre Schmelzpunkte liegen zwischen 50° und 95°. Aus der Schmelze der Hochmolekularen kann man seidenglänzende Fäden ausziehen. Sie lösen sich leicht in Chloroform, Essigester, Aceton, aber schwer in Äther, kaltem Alkohol und in Wasser. Seine Löslichkeit verringert sich beim Bewahren. Die Polyester aus Maleinsäure sind meist farbloses Syrup mit Ausnahme von dem, welcher eine beträchtliche Menge Fumarsäure-Komponent enthält. Ihre durchschnittlichen Molekülgrössen liegen zwischen 450 und 900. Sie sind leicht löslich in Chloroform, und Aceton, besonders leicht in Essigester, aber schwer in kaltem Alkohol, Äther und in Wasser.

Über die Zusammensetzung der Maleinsäure-Ester sei bemerkt, dass der Kohlenstoff-Wert in einigen Fällen (meist d. hohen Reaktionstemperaturen) etwas zu niedrig ausfällt, wenn auch nicht so merklich wie bei den älteren Versuchen.[10] Vielleicht finden sich hier etwa komplizierte Verhältnisse infolge der ungesättigten Kohlenstoff-Bindung.[11]

Räumlicher Bau der Moleküle und Kondensationsvorgänge. Zum Schluss sei kurz über den räumlichen Bau der reagierenden Moleküle, den

(9) Dieser Ausdruck, etwa im Sinne von H. Staudinger, *Z. angew. Chem.*, **42** (1929), 69; vgl. „Die hochmolekularen organischen Verbindungen—Kautschuk und Cellulose," Berlin, 1932, S. 4.

(10) D. Vorländer, *Ann.*, **280** (1894), 167; W. H. Carothers und J. A. Arvin, *J. Am. Chem. Soc.*, **51** (1929), 2560.

(11) Anlagerung von Luftsauerstoff ist hier zu vermuten. Es muss aber durch weitere Versuche bestätigt werden. Über die Anlagerungsfähigkeit des Maleinsäureanhydrids. Siehe z. B. O. Diels u. K. Alder, *Ann.*, **460** (1927), 98; R. Kuhn u. Th. Wagner-Jauregg, *Ber.*, **63 B** (1930), 2662.

Multikondensationsgrad der Produkte und eine Ausbeute erwähnt. Vergleicht man miteinander die Kondensationsreaktionen dieser beiden Säuren mit Äthylenglykol ohne Berücksichtigung der Maleinsäure-Umwandlung, so sieht man aus dem experimentellen Teil entweder bei hoher Temperatur oder bei langer Reaktionsdauer kein grosser Unterschied in der mittleren Molekulargrösse zwischen beiden Reaktionsprodukten, aber man bemerkt eine grössere Ausbeute bei der Fumarsäure als bei der Maleinsäure. In dem Falle, wo die Reaktion bei höherer Temperatur in Gegenwart von Zinkchlorid ausgeführt wird (Umwandlung der Maleinsäure beträchtlich!), wird bei der Maleinsäure ein etwas kleinere Wert der mittleren Molekulargrösse des Reaktionsproduktes gefunden, wenn auch die beiden Ausbeuten beinahe gleich sind.

Überblickt man über die obigen Resultate mit Erwägung des Umstandes, dass im Gegensatz zu Maleinsäure Fumarsäure ganz allmählich in Lösung geht, so könnte man schliessen, dass bei der Fumarsäure eine grössere Neigung zur Bildung der hochmolekularen Kondensationsprodukte beobachtet wird. Der Unterschied ist, glaube ich, entscheidend, wenn auch nie merklich gross ist. Dieses Ergebnis (dass der Unterschied gering ist) ist mir unerwartet, weil, obwohl über eine etwas verschiedene Reaktion, eine solche Beobachtung schon durch Wagner-Jauregg[12] angestellt worden ist, dass Stilben mit Maleinsäure-Anhydrid zu hochmolekularen „Heteropolymerisaten" vereinigt, während die cis-Form, das Iso-Stilben ein solches Polymerisat nur in schlechter Ausbeute ergibt.[13] Um das vorliegende Resultat zu verstehen, dürfte man sich so vorstellen, dass Äthylenglykol selbst eine weitergehende Multikondensation auch bei der Reaktion mit Maleinsäure verursacht habe, indem es in einer etwa trans-Figur,[14] einer zur Kettenbildung

(12) *Ber.*, **63 B** (1930), 3213.

(13) Als diesbezügliche Versuche (über die Konfiguration der Moleküle und die Reaktion) sind auch die Arbeiten von G. Vavon und Mitarbeitern zu nennen, die über die Kinetik der Veresterung von stereoisomeren, einwertigen *o*-Cyclanolen sowie über die der Verseifung ihrer Ester ausgeführt wurden, die ergaben, dass in verschiedenen Fällen die cis-Verbindungen immer langsamer reagieren als die trans-Formen. Zusammenfassend: *Bull. soc. chim.*, [4], **49** (1931), 937.

(14) Dies ist durch Versuche von verschiedenen Seiten bewiesen worden. Durch die bekannten Versuchen von J. Böesekensche Schule nach „Borsäuremethode" (*Ber.*, **46** (1913), 2612; *Rec. trav. chim.*, **40** (1921), 553) sowie nach „Acetonmethode" (Chr. van Loon, Thèse Delft, 1919; J. Böeseken und P. H. Hermans, *Rec. trav. chim.*, **40** (1921), 525; P. H. Hermans, *Z. physik. Chem.*, **113** (1924), 337.), und auch durch das Studium von B. Englund (*J. prak. Chem.*, **122** (1929), 121.) über den Einfluss der Polyoxyverbindungen auf die Löslichkeit der Arsonessigsäure ist so zu schliessen, dass die Hydroxylgruppen in Äthylenglykol eine zur Ringbildung ungünstige Lagerung d. h. die trans-Stellung oder eine ihr ähnliche einnehmen. Ferner aus den Ergebnissen der Dipolforschung lässt sich eine derartige Lagerung der Hydroxylgruppen als wahrscheinlich ableiten. C. T. Zahn, *Physik. Z.*, **33** (1932), 525.

begünstigten Lagerung an der Reaktion teilgenommen hat. Jedoch auf diese Multikondensationsvorgänge mögen neben dem räumliche Bau der beteiligenden Moleküle noch weitere massgebende Einflusse wie z.B. elektrolytische Dissoziation der Säure vorhanden sein.[15] Trotzdem wäre es von grossem Interesse, die Reaktion zwischen dem Diol, welcher als cis-förmig deutlich bewiesen ist, wie z. B. cis 1.2-Cyclopentandiol,[16] und der zweibasischen Säure von cis-Form zu untersuchen,[17] aber da dieser Diol schwer zugänglich ist, ist es mir leider jetzt unmöglich, diese Reaktion weiter zu untersuchen.

Beschreibung der Versuche.

A. Reaktion zwischen Fumarsäure und Äthylenglykol.

Versuch 1. Ein Gemisch von 2.32 g. feingepulverter Fumarsäure (0.02 Mol) und 1.36 g. Äthylenglykol (0.022 Mol) wurde 90 Minuten auf 160–170° erhitzt. Reaktion trat allmählich ein; am Ende blieb etwas Fumarsäure noch ungelöst. Das Reaktionsprodukt wurde mit Wasser einige Male gewaschen. Die ausgeschiedene, weisse Masse wurde in Chloroform aufgenommen, das dabei ungelöste Pulver (hauptsächlich unveränderte Fumarsäure) abfiltriert. Die klare Chloroformlösung wurde mit Wasser gewaschen, mit Na_2SO_4 getrocknet, eingedampft und mit Äther gefällt. Etwas schmierige, weisse Masse. Es wurde bei 70° und dann in Vakuum getrocknet. Schmilzt unscharf bei 68–73°. Ausbeute 1.39 g., d. h. 41% d. Theorie.

Neutralisation: Die Substanz wird in 15 c.c. Aceton gelöst und mit N/50-KOH neutralisiert (Phenolphthalein als Indikator). 0.1068 g. Subst. verbrauchten 6.50 c.c. Kalilauge. Neutralisationsäquivalent 821. Multikondensationsgrad $n=5.65$.

Verseifung: Die soeben neutralisierte Lösung wird mit 15 c.c. N/5-KOH versetzt. Nach 24-stdg. Stehen wird die Lösung zur Ergänzung der Verseifung 15–20 Minuten auf dem Wasserbad erwärmt, und das überschüssige Kali mit N/10-H_2SO_4 zurücktitriert. 17.00 c.c. N/10-H_2SO_4 wurden verbraucht. Verseifungswert/Neutralisationswert $\gamma_{gef.} = 10.00$, $\gamma_{ber.} = 10.30$.

Elementaranalyse: 0.2065 g. Subst. (60 Min. unter 20 mm. Druck, bei 77° getr.) gaben 0.3717 g. CO_2 und 0.0824 g. H_2O. Gefunden: C, 49.09; H, 4.47. Berechnet für $HO-(C_6H_8O_4)_{5.65}-H$ (820.3): C, 49.59; H, 4.41%.

Ebullioskopie: in Aceton. 0.4414 g. Subst. in 15–25.2 c.c. Lösung. $\Delta t=0.053$–$0.076°$. Mol.-Gew. 730–850.

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(15) Über den Einfluss der elektrolytischen Dissoziation der Säure auf die Veresterungsgeschwindigkeit vgl. M. Conrad und C. Brücker, *Z. physik. Chem.*, **7** (1891), 290; H. Goldschmidt, *Ber.*, **29** (1896), 2210; A. Michael, *Ber.*, **42** (1909), 326; ferner A. Kailan, *Z. physik. Chem.*, **87** (1914), 619.

(16) Chr van Loon, Thèse Delft, 1919: J. Böeseken, *Rec. trav. chim.*, **40** (1921), 553. (nach „Borsäuremethode"); P. H. Hermans, *Z. physik. Chem.*, **113** (1924), 337 (nach „Acetonmethode"). vgl. B. Englund, *J. prak. Chem.*, **122** (1929), 121; **129** (1931), 1.

(17) Dabei ist es zu erwarten, dass die Multikondensation nicht so weiter schreiten werde.

Versuch 2. 1 Mol Fumarsäure+1.05 Mol Äthylenglykol. Reaktionsdauer 4 Stunden. Reaktionstemperatur 170–180°. Produkt weisses Pulver. Beim Erhitzen erweicht es bei 80° und schmilzt hauptsächlich bei 95–97°. Ausbeute 68% d. Theorie.

Neutralisation und Verseifung: Neutralisationsäquivalent 1043. Multikondensationsgrad $n=7.21$. Verseifungswert/Neutralisationswert $\gamma_{gef.} = 13.13$, $\gamma_{ber.} = 13.42$.

Elementaranalyse: Gefunden: C, 50.07; H, 4.60. Berechnet für $HO-(C_6H_6O_4)_{7.21}-H$ (1043): C, 49.81; H, 4.38%.

Ebullioskopie: in Aceton. Mol.-Gew. 1020–1260.

Versuch 3. 1 Mol Fumarsäure+1.1 Mol Äthylenglykol. Reaktionsdauer 3.5 Stunden. Reaktionstemperatur 155–160°. Produkt schwachgelbliches weisses Pulver. Schmelzpunkt 74–76°. Ausbeute 52% d. Theorie.

Neutralisation und Verseifung: Neutralisationsäquivalent 954. Multikondensationsgrad $n=6.59$. Verseifungswert/Neutralisationswert $\gamma_{gef.} = 11.50$, $\gamma_{ber.} = 12.18$.

Elementaranalyse: Gefunden: C, 48.86; H, 4.68. Berechnet für $HO-(C_6H_6O_4)_{6.59}-H$ (954): C, 49.73; H, 4.39%.

Ebullioskopie: in Aceton. Mol.-Gew. 920–970.

Versuch 4. 1 Mol Fumarsäure+1.1 Mol Äthylenglykol. 2 Stunden auf 140–150°, dann 7 Stunden auf 160–165° erhitzt. Produkt gelblichweisses Pulver. Schmelzpunkt 92–95°. Ausbeute 67% d. Theorie.

Neutralisation und Verseifung: Neutralisationsäquivalent 1212. Multikondensationsgrad $n=8.41$. Verseifungswert/Neutralisationswert $\gamma_{gef.} = 15.15$, $\gamma_{ber.} = 15.81$.

Elementaranalyse: Gefunden: C, 49.83; H, 4.52. Berechnet für $HO-(C_6H_6O_4)_{8.41}-H$ (1212.6): C, 49.77; H, 4.35%.

Ebullioskopie: in Aceton. Mol.-Gew. 1220–1480.

Versuch 5. 1 Mol Fumarsäure+1.1 Mol Äthylenglykol+0.5 Mol $ZnCl_2$. Reaktionsdauer 60 Minuten. Reaktionstemperatur 150–160°.

Die Reaktion wurde durch $ZnCl_2$ beschleunigt: schon nach 30 Minuten-Erhitzen wurde Fumarsäure nahezu in Lösung gebracht. Die Reaktionsmasse war in der Hitze eine klare Schmelze, in der Kälte eine harte undurchsichtige Masse. Dies wurde mit Wasser einigemal gewaschen, in $CHCl_3$ aufgenommen, wobei unveränderte Fumarsäure ungelöst blieb. Die $CHCl_3$-Lösung wurde mehrmals mit Wasser geschüttelt, wodurch $ZnCl_2$ völlig entfernt wurde, mit Na_2SO_4 getrocknet und verdampft.

Der Rückstand bildet eine schmierige weisse Masse von unscharfem Schmelzpunkt 50–60°. Ausbeute 35% d. Theorie.

Neutralisation und Verseifung: Neutralisationsäquivalent 685. Multikondensationsgrad $n=4.70$. Verseifungswert/Neutralisationswert $\gamma_{gef.} = 8.10$, $\gamma_{ber.} = 8.40$.

Elementaranalyse: Gefunden: C, 48.12, 48.29; H, 4.73, 4.70. Berechnet für $HO-(C_6H_6O_4)_{4.70}-H$ (685.6): C, 49.35; H, 4.44%.

Versuch 6. 1 Mol Fumarsäure+1.1 Mol Äthylenglykol+0.5 Mol $ZnCl_2$. Beim Erhitzen dieses Gemisches 90 Minuten auf 165–170° wurde ein harziges, etwas gefärbtes Reaktionsprodukt (Molekulargewicht ca. 650) erhalten mit einer Ausbeute 24% d. Theorie.

Aus den Versuchen 5 und 6 sieht man auch eine degenerierende Wirkung von $ZnCl_2$ bei hoher Temperatur.

Versuch 7. 3.48 g. Fumarsäure (0.03 Mol) und *überschüssiges* Äthylenglykol (0.062 Mol) wurden mit 2.57 g. geschmolzenem Zinkchlorid 60 Minuten auf 135–140°

erhitzt. Am Ende war Fumarsäure nahezu in Lösung. Das flüssige Reaktionsgemisch wurde in Wasser gegossen, die ausgeschiedene, weisse Masse mit Wasser verrieben, und dann wie bei Versuch 5 bearbeitet. Produkt eine weisse schmierige Masse vom Schmelzpunkt 54–57°. Ausbeute 0.62 g.

Neutralisation und Verseifung: Neutralisationsäquivalent 998. Verseifungswert/Neutralisationswert $\gamma_{gef.} = 11.95$.

Ebullioskopie: in Aceton, Mol.-Gew. 608–680.

Elementaranalyse: Gefunden: C, 48.82; H, 4.82%.

Wenn man diesen sauren Ester einbasisch annimmt, so wird der Multikondensationsgrad (n) als 6.90 berechnet. Daraus folgt: $\gamma_{ber.} = 12.80$. Diese Abweichungen von den experimentellen Ergebnissen zeigen, dass ein Gemenge von neutralem und saurem Polyester von dem Molekulargewicht ca. 650 vorliegt. Wählt man zu dem Mengeverhältnis der beiden Ester 1:2, so treffen die berechneten Werte ($\gamma_{ber.} = 12.00$, C=49.37, H=4.56%) mit den gefundenen zusammen.

B. Reaktion zwischen Maleinsäure und Äthylenglykol.

Versuch 1. Ein Gemisch von 6.96 g. Maleinsäure (0.06 Mol) und 3.72 g. Äthylenglykol (0.06 Mol) wurde mit 2.25 g. geschmolzenem Zinkchlorid 55 Minuten auf 115–120° erhitzt. Das klare Reaktionsprodukt wurde in Wasser gegossen, die ausgeschiedene, halbfeste Masse zweimal mit Wasser verrieben, wodurch die unveränderten Ausgangsstoffe sowie $ZnCl_2$ grösstenteils entfernt wurden, und der Rückstand in Essigester aufgenommen. Die Essigesterlösung wurde mit Wasser zweimal gewaschen, mit Na_2SO_4 getrocknet und verdampft. Der Rückstand bildet ein farbloses, zähes Syrup. Ausbeute 1.04 g., d. h. 12% d. Theorie.

Neutralisation: 0.0542 g. Subst. in 5 c.c. Acetonlösung verbrauchten 5.55 c.c. N/50-KOH. Neutralisationsäquivalent 488. Multikondensationsgrad $n=3.31$.

Verseifung: Die oben neutralisierte Lösung verbrauchte zur Verseifung 3.10 c.c. N/5-KOH. Verseifungswert/Neutralisationswert $\gamma_{gef.} = 5.58$, $\gamma_{ber.} = 5.62$.

Elementaranalyse: 0.1079 g. Subst (30 Min. in Vakuum bei 77°, über P_2O_5 getr.) gaben 0.1950 g. CO_2 und 0.0436 g. H_2O. Gefunden: C, 49.28; H, 4.52. Berechnet für $HO-(C_6H_6O_4)_{2.31}-H$ (488.2): C, 48.80; H, 4.52%.

Ebullioskopie: 0.1503 g. Subst. in 17–23 c.c. Aceton. $\Delta t = 0.030–0.037°$. Mol.-Gew. 480–530.

Fumarsäure-Gehalt: Die Menge der durch Umwandlung entstandenen Fumarsäure in den Polyestern aus Maleinsäure wurde nach zwei Methoden abgeschätzt: die ein Methode a) stammt von D. Vorländer,[18] der zeigte, dass sich die beiden genannten Säuren in den Kristallwasser-Gehalt des gut kristallisierbaren Bariumsalzes voneinander unterscheiden, damit kann man die Fumarsäuremenge abschätzen durch Bestimmung des Ba-Gehaltes von dem durch Verseifung erhaltenen Bariumsalz-Gemisch; die andere b) ist eine nach Hahn-Haarmann,[19] deren Prinzip auf die direkte Wägung des für Fumarsäure charakteristischen, schwerlöslichen Merkuro-Salzes beruht.

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(18) *Ann.*, **280** (1894), 167.

(19) A. Hahn und W. Haarmann, *Z. Biol.*, **87** (1928), 107; *ibid.*, **89** (1929), 159. vgl. A. Ölander, *Z. physik. Chem.*, [A], **144** (1929), 49; H. Meyer, „Nachweis und Bestimmung der org. Verbindungen," Berlin, 1933, S. 141.

a) *nach Bariummethode.* Die Bereitung des Ba-Salzes habe ich folgenderweise ausgeführt: der Polyester wird durch halbstündiges Erwärmen mit N/5-KOH verseift, überschüssiges Kali mit N/10-HCl neutralisiert, und mit einer berechneten Menge 1 N-$BaCl_2$ versetzt; beim Verdampfen der Lösung scheidet das Ba-Salz als schöne Kristallen aus. 0.0956 g. Ba-Salz (lufttrocken) gaben 0.0815 g. $BaSO_4$. Gefunden: Ba, 50.3. Berechnet für $C_4H_2O_4Ba+H_2O$ (Maleinat): Ba, 50.93, für $C_4H_2O_4Ba+3H_2O$ (Fumarat): 44.91%. Daraus Fumarsäure: ca. 10% d. Gesamtsäure.

b) *nach Merkurosalzmethode:* Der Polyester wird wie bei a) verseift, das überschüssige Kali mit N/5-HNO_3 neutralisiert, und dazu Fällungsreagenz hinzugefügt. Der Niederschlag wird nach 1-tägigem Stehen durch Glasfilter filtriert, gewaschen, und bei 70° getrocknet. 0.1658 g. Ester gaben 0.0534 g. Merkuro-Fumarat. Daraus Fumarsäure-Gehalt des Polyesters: 9.7%. (entsprechend 12.2% d. Gesamtsäure.)

Versuch 2. 1 Mol Maleinsäure + 1 Mol Äthylenglykol. Reaktionsdauer 4 Stunden. Reaktionstemperatur 120–126°. Produkt schwach braungefärbtes Harz. Ausbeute 14% d. Theorie.

Neutralisation und Verseifung: Neutralisationsäquivalent 510. Multikondensationsgrad $n=3.46$. Verseifungswert/Neutralisationswert $\gamma_{gef.} = 5.90$, $\gamma_{ber.} = 5.92$.

Elementaranalyse: Gefunden: C, 48.78; H, 4.75. Berechnet für HO–$(C_6H_8O_4)_{3.46}$–H (509.5): C, 48.89; H, 4.51%.

Ebullioskopie: in Aceton. Mol.-Gew. 450–560.

Fumarsäure-Gehalt: a) *nach Bariummethode.* Gefunden: Ba, 50.7%. Fumarsäure: ca. 5% d. Gesamtsäure. b) *nach Merkurosalzmethode.* Gefunden: Fumarsäure-Gehalt im Ester 5.6% (entsprechend 7.1% d. Gesamtsäure.)

Versuch 3. 1 Mol Maleinsäure+1.1 Mol Äthylenglykol. Reaktionsdauer 60 Minuten. Reaktionstemperatur 155–160°. Produkt farbloses Harz. Ausbeute 18.5% d. Theorie.

Neutralisation und Verseifung: Neutralisationsäquivalent 457. Multikondensationsgrad $n=3.09$. Verseifungswert/Neutralisationswert $\gamma_{gef.} = 5.14$, $\gamma_{ber.} = 5.18$.

Elementaranalyse: Gefunden: C, 48.78; H, 4.60. Berechnet für HO–$(C_6H_8O_4)_{3.09}$–H (457.0): C, 48.69; H, 4.53%.

Ebullioskopie: in Aceton. Mol.-Gew. 500–560.

Fumarsäure-Gehalt: a) *nach Bariummethode.* Gefunden: Ba, 48.0%. Fumarsäure: ca 45% d. Gesamtsäure. b) *nach Merkurosalzmethode.* Gefunden: Fumarsäure-Gehalt im Ester 16.3% (entsprechend 20.8% d. Gesamtsäure.)

Versuch 4. 1 Mol Maleinsäure+1 Mol Äthylenglykol+0.5 Mol $ZnCl_2$. Reaktionsdauer 3 Stunden. Reaktionstemperatur 115–120°. Das entstandene, weisse, zähe Harz wurde zweimal mit Wasser verrieben, in Essigester aufgenommen, mit Wasser mehrmals gewaschen, mit Na_2SO_4 getrocknet, und mit Äther gefällt. Farbloses Harz. Ausbeute 24% d. Theorie.

Neutralisation und Verseifung: Neutralisationsäquivalent 659. Multikondensationsgrad $n=4.51$. Verseifungswert/Neutralisationswert $\gamma_{gef.} = 7.92$, $\gamma_{ber.} = 8.02$.

Elementaranalyse: Gefunden: C, 48.43; H, 4.68. Berechnet für HO–$(C_6H_8O_4)_{4.51}$–H (659.0): C, 49.30; H, 4.45%.

Ebullioskopie: in Aceton. Mol.-Gew. 590–660.

Fumarsäure-Gehalt: a) *nach Bariummethode.* Gefunden: Ba, 46.0%. Fumarsäure: ca. 80% d. Gesamtsäure. b) *nach Merkurosalzmethode.* Fumarsäure-Gehalt im Ester 53.9%. (entsprechend 67.8% d. Gesamtsäure.)

Im folgenden werden die Versuche beschrieben, die unter gleichen Bedingungen bei Fumarsäure ausgeführt wurden, wenn auch solche Bedingungen für Maleinsäure allzu heftig sind.

Versuch 5. 1 Mol Maleinsäure+1.1 Mol Äthylenglykol. Reaktionsdauer 90 Minuten. Reaktionstemperatur 160–170°. (Vergleich mit Fumarsäure-Versuch 1.) Die entstandene, klare Schmelze wurde in Wasser verrieben, das ausgeschiedene, farblose Öl in $CHCl_3$ gelöst. Die Lösung wurde mit Wasser zweimal gewaschen, mit Na_2SO_4 geklärt und verdampft. Farbloses Harz. Ausbeute 31% d. Theorie.

Neutralisation und Verseifung: Neutralisationsäquivalent 891. Multikondensationsgrad $n=6.15$. Verseifungswert/Neutralisationswert $\gamma_{gef.} = 11.24$, $\gamma_{ber.} = 11.30$.

Elementaranalyse: Gefunden: C, 48.73; H, 4.52. Berechnet für $HO-(C_6H_6O_4)_{6.15}-H$ (891.6): C, 49.66; H, 4.40%.

Ebullioskopie: in Aceton. Mol.-Gew. 830–910.

Fumarsäure-Gehalt: a) *nach Bariummethode.* Gefunden: Ba, 49.8%. Fumarsäure: ca. 20% d. Gesamtsäure. b) *nach Merkurosalzmethode.* Gefunden: Fumarsäure-Gehalt im Ester 23.1% (entsprechend 28.9% d. Gesamtsäure.)

Versuch 6. 1 Mol Maleinsäure+1 Mol Äthylenglykol+0.5 Mol Zinkchlorid. Reaktionsdauer 60 Minuten. Reaktionstemperatur 150–160°. (Vergleich mit Fumarsäure-Versuch 5.) Das entstandene, schwachgelbliche, ziemlich feste Reaktionsprodukt wurde mit Wasser gut gewaschen. Der $CHCl_3$-Extrakt wurde mit Wasser geschüttelt, mit Na_2SO_4 geklärt, und verdampft; dieser Reinigungsprozess nochmal wiederholt. Schmierige, weisse Masse. Schmilzt hauptsächlich bei 52–55°. Ausbeute 34% d. Theorie.

Neutralisation und Verseifung: Neutralisationsäquivalent 562. Multikondensationsgrad $n=3.84$. Verseifungswert/Neutralisationswert $\gamma_{gef.} = 6.54$, $\gamma_{ber.} = 6.62$.

Elementaranalyse: Gefunden: C, 48.30; H, 4.73. Berechnet für $HO-(C_6H_6O_4)_{3.84}-H$ (563.5): C, 49.06, 49.06; H, 4.48%.

Fumarsäure-Gehalt: a) *nach Bariummethode.* Gefunden: Ba, 45.8%. Fumarsäure: ca. 85% d. Gesamtsäure. b) *nach Merkurosalzmethode.* Fumarsäure-Gehalt im Ester 56.8%. (entsprechend 71.7% d. Gesamtsäure.)

Versuch 7. Beim Erhitzen von 3.48 g. Maleinsäure (0.03 Mol) und 2.05 g. Äthylenglykol (0.033 Mol) 3.5 Stdn. auf 155–160° wurden 2.22 g. schwachgelbes, zähes Harz gewonnen. (Extraktionsmittel $CHCl_3$) Ausbeute 51% d. Theorie. (Vergleich mit Fumarsäure-Versuch 3.)

Neutralisation und Verseifung: Neutralisationsäquivalent 919. Multikondensationsgrad $n=6.34$. Verseifungswert/Neutralisationswert $\gamma_{gef.} = 11.39$, $\gamma_{ber.} = 11.68$.

Elementaranalyse: Gefunden: C, 47.87, 47.92, 48.19; H, 4.43, 4.53, 4.47. Berechnet für $HO-(C_6H_6O_4)_{6.34}-H$ (918.6): C, 49.69; H, 4.39%.

Ebullioskopie: in Aceton. Mol.-Gew. 694–746.

Fumarsäure-Gehalt: a) *nach Bariummethode.* Gefunden: Ba, 48.8%. Fumarsäure: ca. 35% d. Gesamtsäure. b) *nach Merkurosalzmethode.* Fumarsäure-Gehalt im Ester 27.6% (entsprechend 34.5% d. Gesamtsäure.)

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A SPECTROGRAPHIC METHOD FOR THE STUDY OF UNSTABLE COMPOUNDS IN EQUILIBRIUM.

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Introduction. As early as 1921 Professor Y. Shibata established a spectroscopic method for the detection of the formation of complex salts in dilute solution.[1] This method consists in preparing a set of solutions, in which initial concentrations of the components of the molecular compound have simple ratio to each other, and comparing the absorption spectra of these solutions. The ratio of initial concentrations of the components in the solution, which gives the strongest end absorption, shows the ratio of combination of the components to form the molecular compound. Four years later P. Job[2] also proposed a similar method.

The present paper deals with a quantitative extension of Prof. Shibata's method in finding composition of unstable compounds and at the same time proposes a general method for the study of chemical equilibrium, determining the equilibrium constant, concentration of unstable compounds, as well as extinction coefficients of the compounds whose spectra are not obtainable without superposition of those of other substances.

The Method. (1) Two substances, A and B, react with each other in dilute solution to form an unstable compound whose composition is unknown.

$$mA + nB \rightleftarrows A_mB_n .$$

$$K = \frac{[A_m B_n]}{[A]^m [B]^n} , \quad \cdots\cdots\cdots\cdots\cdots\cdots (1)$$

where m and n are unknown.

Let the initial concentrations of A and B be a and b respectively, and the concentration of the compound (C) x.

$$K = \frac{x}{(a-mx)^m (b-nx)^n} . \quad \cdots\cdots\cdots\cdots (1')$$

Also let the extinction coefficients of A, B and A_mB_n for a wave-length λ_1 be ε_1^A, ε_1^B and ε_1^C respectively, then

(1) Y. Shibata, T. Inoue, and Y. Nakatsuka, *J. Chem. Soc. Japan*, **42** (1921), 983; *Japanese J. Chem.*, **1**, (1922), 1; *Chem. Abst.*, **16** (1922), 2075.

(2) P. Job, *Compt. rend.*, **180** (1925), 928; **182** (1926), 1622; *Ann. chim.*, **9** (1928), 143.

$$E_1 = \Sigma\varepsilon c = \varepsilon_1^{\mathrm{A}}(a-mx)+\varepsilon_1^{\mathrm{B}}(b-nx)+\varepsilon_1^{\mathrm{C}}x\ , \quad \cdots\cdots\cdots (2)$$

where E_1 is measurable absorption of the equilibrium mixture, representing $\Sigma\varepsilon c$ in

$$I = I_0 \times 10^{-\Sigma\varepsilon cd}\ .$$

Therefore

$$x = \frac{E_1-\varepsilon_1^{\mathrm{A}}a-\varepsilon_1^{\mathrm{B}}b}{\varepsilon_1^{\mathrm{C}}-m\varepsilon_1^{\mathrm{A}}-n\varepsilon_1^{\mathrm{B}}}\ . \quad \cdots\cdots\cdots\cdots (3)$$

For another wave-length λ_2 and for the same solution,

$$x = \frac{E_2-\varepsilon_2^{\mathrm{A}}a-\varepsilon_2^{\mathrm{B}}b}{\varepsilon_2^{\mathrm{C}}-m\varepsilon_2^{\mathrm{A}}-n\varepsilon_1^{\mathrm{B}}}\ . \quad \cdots\cdots\cdots\cdots (3')$$

From (3) and (3′)

$$(E_2-\varepsilon_2^{\mathrm{A}}a-\varepsilon_2^{\mathrm{B}}b)\varepsilon_1^{\mathrm{C}}-(E_1-\varepsilon_1^{\mathrm{A}}a-\varepsilon_1^{\mathrm{B}}b)\varepsilon_2^{\mathrm{C}}+\left\{(E_1-\varepsilon_1^{\mathrm{A}}a-\varepsilon_1^{\mathrm{B}}b)\varepsilon_2^{\mathrm{A}}-(E_2-\varepsilon_2^{\mathrm{A}}a-\varepsilon_2^{\mathrm{B}}b)\varepsilon_1^{\mathrm{A}}\right\}m$$

$$+\left\{(E_1-\varepsilon_1^{\mathrm{A}}a-\varepsilon_1^{\mathrm{B}}b)\varepsilon_2^{\mathrm{B}}-(E_2-\varepsilon_2^{\mathrm{A}}a-\varepsilon_2^{\mathrm{B}}b)\varepsilon_1^{\mathrm{B}}\right\}n = 0\ . \quad \cdots\cdots\cdots (4)$$

As $\varepsilon_1^{\mathrm{A}}$, $\varepsilon_2^{\mathrm{A}}$, $\varepsilon_1^{\mathrm{B}}$ and $\varepsilon_2^{\mathrm{B}}$ may be obtained by measurements of spectra of A and B, all the terms in brackets are known or measurable values and the equation (4) may be expressed as

$$\left.\begin{aligned} & p\varepsilon_1^{\mathrm{C}}-q\varepsilon_2^{\mathrm{C}}+rm+sn = 0\ , \\ \text{where}\quad & p = E_2-\varepsilon_2^{\mathrm{A}}a-\varepsilon_2^{\mathrm{B}}b\ , \\ & q = E_1-\varepsilon_1^{\mathrm{A}}a-\varepsilon_1^{\mathrm{B}}b\ , \\ & r = q\varepsilon_2^{\mathrm{A}}-p\varepsilon_1^{\mathrm{A}}\ , \\ \text{and}\quad & s = q\varepsilon_2^{\mathrm{B}}-p\varepsilon_1^{\mathrm{B}}\ . \end{aligned}\right\} \quad \cdots\cdots\cdots\cdots (4')$$

For various combinations of a and b, the following set of equations are obtained:

$$\left.\begin{aligned} & p_1\varepsilon_1^{\mathrm{C}}-q_1\varepsilon_2^{\mathrm{C}}+r_1m+s_1n = 0 \\ & p_2\varepsilon_1^{\mathrm{C}}-q_2\varepsilon_2^{\mathrm{C}}+r_2m+s_2n = 0 \\ & \cdots\cdots\cdots\cdots \\ & \cdots\cdots\cdots\cdots \\ & p_N\varepsilon_1^{\mathrm{C}}-q_N\varepsilon_2^{\mathrm{C}}+r_Nm+s_Nn = 0 \end{aligned}\right\} \quad \cdots\cdots\cdots\cdots (5)$$

By the method of least squares, $\frac{\varepsilon_1^C}{n}$, $\frac{\varepsilon_2^C}{n}$ and $\frac{m}{n}$ may be determined. Being usually small integers, m and n may easily be found from the ratio of m to n, e.g., for $\frac{m}{n} = 0.67$, $m = 2$ and $n = 3$, etc. Consequently ε_1^C and ε_2^C are found. Repeating the above process for various wave-lengths, extinction coefficients and the absorption curve of the unstable compound are obtained.

Substituting these values of ε_1^C, ε_2^C, m, n, etc. in (3), (3′), etc., we can find the concentrations of the compound, from which the equilibrium constant K is calculated.

It is, however, difficult to find the ratio of m to n, if the absorption coefficients of component substances are very small compared with those of the compound. In such cases m and n may conveniently be determined by a spectrographic method similar to the original works of Prof. Y. Shibata.

(2) If both the components, A and B, give no appreciable absorption in spectral regions in which the compound shows absorption, the following method is adopted.

The method consists in preparing a series of mixed solutions, in which initial concentrations of A and B vary to have simple ratio to each other, keeping their sum constant, and measuring the absorption of these solutions. Then the ratio of the initial concentrations of the mixed solution, which gives the highest absorption for the molecular compound, is the ratio of combination, because the maximum concentration for the compound is attained when the ratio of the initial concentrations of the components is exactly the ratio of combination to form the compound. This fact can be proved simply as follows.

From
$$\frac{x}{(a-mx)^m(b-nx)^n} = K,$$

and
$$a + b = \text{constant},$$

$$\frac{dx}{da} = \frac{K(a-mx)^{m-1}(b-nx)^{n-1}(mb-na)}{1+K\{m^2(a-mx)^{m-1}(b-nx)^n + n^2(a-mx)^m(b-nx)^{n-1}\}}.$$

The condition for the maximum value of x is given by

$$\frac{dx}{da} = 0, \quad \text{i.e.} \quad \frac{a}{b} = \frac{m}{n}.$$

Prof. Y. Shibata applied this principle only to end absorption in ultraviolet region. It is, however, clear that this principle can be applied to any absorption bands.

(3) If the absorption of one of the components overlaps the absorption of the compound, i.e., the other component only gives no appreciable absorption in spectral parts in which the compound shows absorption bands, it is difficult to find the highest concentration of the compound directly from comparison of a set of absorption curves prepared as in the previous case (2).

Suppose two cases (I and I′) of different initial concentrations, a and a' for A component and b and b' for B component, and let the concentrations of the compound C be x and x' respectively,

$$\frac{x}{(a-mx)^m(b-nx)^n} = \frac{x'}{(a'-mx')^m(b'-nx')^n} .$$

Also let extinction coefficients of B and C at wave-lengths λ_1 and λ_2 be ε_1^B, ε_2^B, ε_1^C and ε_2^C, the component A giving no appreciable absorption at these wave-lengths. The absorption for these cases (I and I′) is represented in Fig. 1.

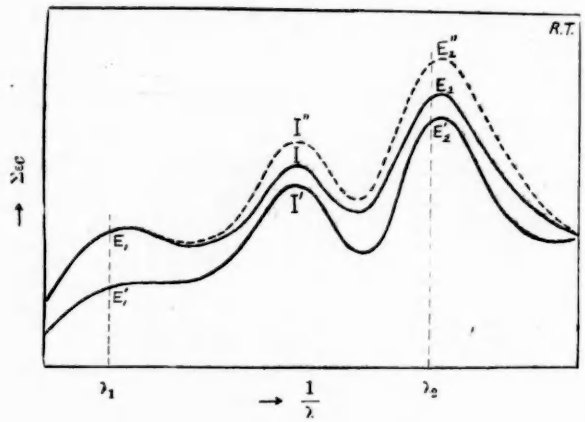

Fig. 1.

At λ_1 and λ_2

$$E_1 = \varepsilon_1^B(b-nx)+\varepsilon_1^C x . \qquad E_2 = \varepsilon_2^B(b-nx)+\varepsilon_2^C x .$$

$$E_1' = \varepsilon_1^B(b'-nx')+\varepsilon_1^C x'. \qquad E_2' = \varepsilon_2^B(b'-nx')+\varepsilon_2^C x'.$$

The difference of $\Sigma\varepsilon c$ at λ_1

$$a_1 = E_1-E_1' = \varepsilon_1^B\left\{(b-nx)-(b'-nx')\right\}+\varepsilon_1^C(x-x') .$$

The concentration of B corresponding to this absorption difference $\delta = (b-nx)-(b'-nx')+\frac{\varepsilon_1^C}{\varepsilon_1^B}(x-x')$. The absorption which should be given by this quantity of B is added throughout the curve I'. The curve thus drawn is shown as I'' in Fig. 1.

Then the addition to I' at λ_2

$$a_2 = \varepsilon_2^B\left\{(b-nx)-(b'-nx')\right\}\frac{\varepsilon_1^C\varepsilon_2^B}{\varepsilon_1^B}(x-x') .$$

$$\therefore \quad E_2'' = E_2'+a_2 = \varepsilon_2^B(b-nx)+\varepsilon_2^Cx'+\frac{\varepsilon_1^C\varepsilon_2^B}{\varepsilon_1^B}(x-x') ,$$

therefore

$$E_2''-E_2 = \frac{\varepsilon_1^B\varepsilon_2^C-\varepsilon_1^C\varepsilon_2^B}{\varepsilon_1^B}(x'-x)$$

$$E_2''-E_2 \propto x'-x \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

The difference between the curves I and I'' is proportional to the difference of concentrations of C.

This principle affords the means of comparing concentrations of the compound in equilibrium with other substances. Absorption is measured with a series of mixed solutions, in which initial concentrations vary, keeping the sum constant. To the curves of Σec, calculated absorption of B is added to make total absorption in all cases the same at one wave-length, and then the heights of the curves at another wave-length are compared. Then the height-differences are proportional to the concentration-differences for the compound in question. The solution corresponding to the highest curve at the wave-length of comparison is of the highest concentration in C and the ratio of the initial concentrations for this solution gives the ratio of combination of A and B to form C. The equalization and comparison may theoretically be executed at any wave-lengths, but, for practical purpose, it is convenient to choose some particular wave-lengths. In order to facilitate the comparison, i.e., to make the difference $E_2''-E_2$ larger, the wave-lengths should be chosen so that the proportionality constant in the relation (6) may attain the highest possible absolute value. This condition may be fulfiled when

1) ε_1^B and ε_2^C are as large as possible, and ε_1^C and ε_2^B are as small as possible, or 2) vice versa.

In practice, therefore, the wave-lengths of absorption bands are preferably adopted as the points of equalization and comparison. An example of this method is given hereunder.

The Example: The Complex Salt Formation between Potassium Iodide and Iodine. This reaction has been investigated by many authors in various directions, the existence of complex compounds being proved by researches on freezing point depression,[3] solubility,[4] diffusion,[5] conductivity,[6] vapour pressure,[7] adsorption,[8] partition of iodine between two solvents,[9] as well as absorption spectra.[10]

The compositions of these complex compounds are known, but the experiment was carried out as if they were unknown. It is simply because the example is given for the purpose of showing the general procedure of this method.

The equilibrium constant was determined by several authors by measuring vapour pressure,[11] conductivity,[12] partition of iodine in different solvents[13] or solubility.[14]

Of these methods, those which deal with vapour pressure, solubility or partition can be applied only for special cases and are not suitable for general use in studying equilibrium. Compared with these methods, the conductivity method is of more general application, but is apt to suffer a

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great deal from the error caused by the slightest contamination of impurities. On the contrary, the spectrographic method here proposed is more direct than those which consist in measuring partition, vapour pressure, etc. and moreover it is safer than the conductivity method so long as the characteristic absorption bands are the object of the measurement. The spectroscopic method proposed by P. Job,[15] deals only with absorption limit and is not adequate for quantitative calculation of equilibrium constant, etc.

Absorption of mixed solutions of potassium iodide and iodine was photographed with a Spekker photometer and a Hilger spectrograph. Special precaution was taken to avoid photochemical reactions making the time of exposure as short as possible and changing solutions frequently. As the concentration is very small throughout the experiment and total ionization and complete hydration may reasonably be assumed, there is no need of considering change of absorption due to these effects. The absorption of these solutions is shown in Fig. 2 (I, II, III, IV, V and VI) together with the absorption of potassium iodide (A) and iodine (B).

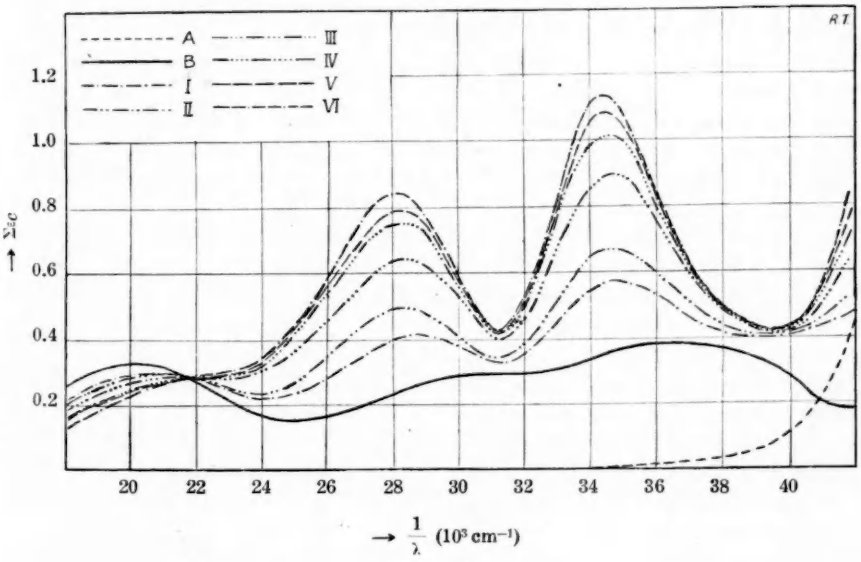

Fig. 2.

(15) *Loc. cit.*

The absorption is shown by plotting $\Sigma\varepsilon c$ against wave-number. The initial concentration of potassium iodide a and iodine b, together with E at wave numbers, 20×10^3, 28×10^3, and 34.5×10^3, are given in Table 1.

Table 1. (cf. Fig. 2)

Curve	$a:b$	$a(10^{-5}$mol/l.)	$b(10^{-5}$mol/l.)	d(cm.)	E		
					20×10^3	28×10^3	34.5×10^3
A		100.0	0.0	20			
B		0.0	10.8	1	0.34	0.24	0.36
I	1 : 2	5.0	10.8	1	0.30	0.40	0.57
II	2 : 2	10.0	10.8	1	0.29	0.49	0.67
III	3 : 2	15.0	10.8	1	0.27	0.64	0.89
IV	4 : 2	20.0	10.8	1	0.24	0.75	1.02
V	5 : 2	25.0	10.8	1	0.24	0.79	1.08
VI	6 : 2	30.0	10.8	1	0.22	0.85	1.13

Fig. 2 and Table 1 plainly show that the maximum at 20×10^3 belongs to iodine and the other two maxima at 28×10^3 and 34.5×10^2 to the compound between potassium iodide and iodine. At 22×10^3 all the solutions have the same absorption. It shows that iodine and the compound have the same extinction coefficient at this wave-length. It is also obvious from the curve A that potassium iodide gives no appreciable absorption at the points of absorption maxima of either iodine or the compound. This is exactly the case corresponding to (3) on p. 30.

In order to find m and n empirically, absorption of another series of solutions was measured, varying initial concentrations of potassium iodide and iodine, and at the same time keeping the sum constant. The absorption is shown in Fig. 3.

In Fig. 3 the curves XI, XII, and XIII show the highest absorption in spectral regions of absorption bands of the compound, but it is also clear that these solutions contain more iodine than the rest of the solutions.

E_1 at wave number 20×10^3 is measured. The differences of E_1's are shown in Table 3 as α_1 and δ is the corresponding quantity of iodine. α_2 shows the addition at wave number 34.5×10^3. Then E_2 at the same wave number plus α_2 gives E_2''.

Fig. 4 shows the curves after the graphical addition. Differences of these curves are theoretically proportional to the differences of concentrations of the molecular compound as we have shown above in the relation (6). We can, therefore, plainly see from these curves that the molar ratio of

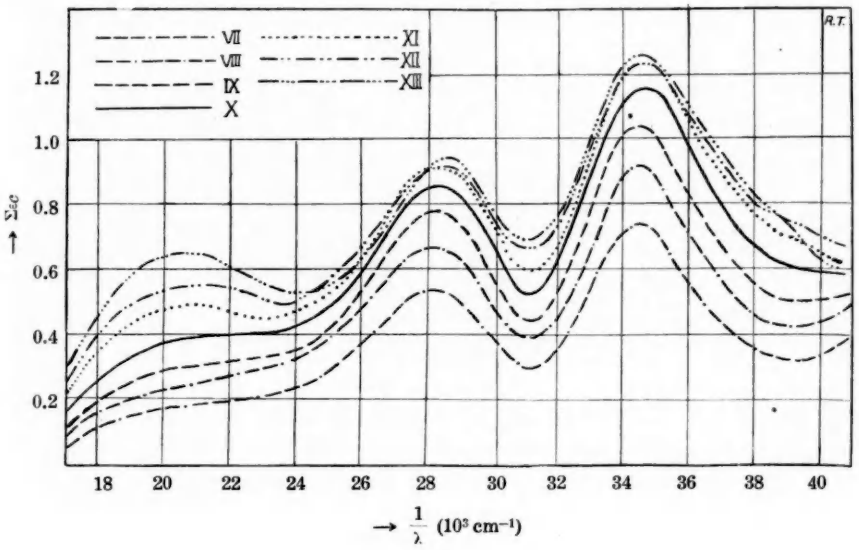

Fig. 3.

Table 2. (cf. Fig. 3)

Curve	$a:b$	$a(10^{-5}$mol/l.)	$b(10^{-5}$mol/l.)	d(cm.)	E		
					20×10^3	28×10^3	34.5×10^3
VII	3 : 1	22.5	7.5	1	0.18	0.54	0.74
VIII	2 : 1	20.0	10.0	1	0.22	0.66	0.90
IX	3 : 2	18.0	12.0	1	0.29	0.77	1.04
X	1 : 1	15.0	15.0	1	0.37	0.84	1.14
XI	2 : 3	12.0	18.0	1	0.48	0.90	1.23
XII	1 : 2	10.0	20.0	1	0.55	0.90	1.23
XIII	1 : 3	7.5	22.5	1	0.64	0.91	1.25

Table 3. (Fig. 3 and Fig. 4)

Curve	E_1	E_2	α_1	$\delta(10^{-5}$mol/l.)	α_2	E_2''
	20×10^3	34.5×10^3				
VII	0.18	0.74	0.46	14.6	0.47	1.21
VIII	0.22	0.90	0.42	13.3	0.43	1.33
IX	0.29	1.04	0.35	11.1	0.36	1.40
X	0.37	1.14	0.27	8.6	0.28	1.42
XI	0.48	1.23	0.16	5.1	0.16	1.39
XII	0.55	1 23	0.09	2.9	0.09	1.33
XIII	0.64	1.25	0.00	0.0	0.00	1.25

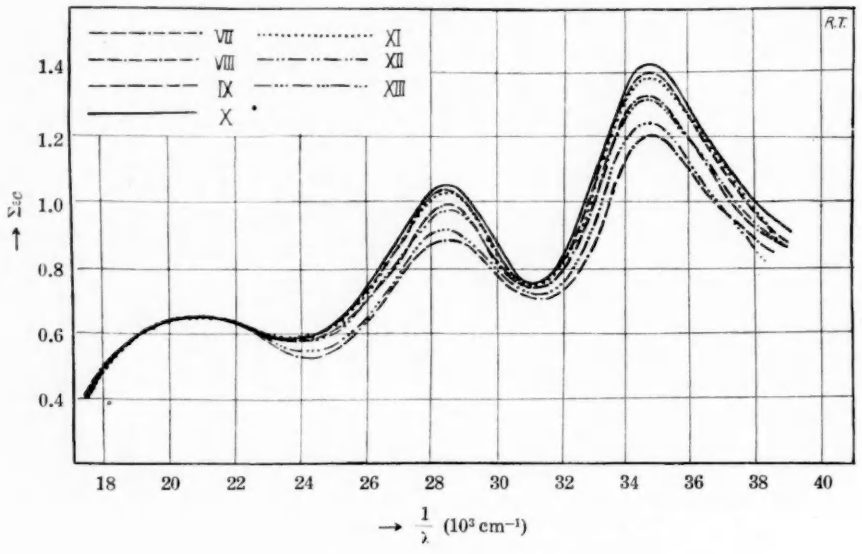

Fig. 4.

combination between potassium iodide and iodine, in our case, is one to one, as the curve X gives the highest absorption at wave numbers 28×10^3 and 34.5×10^3, which correspond to the absorption bands of the molecular compound. Thus m and n are found to be 1 and 1, the formula for the molecular compound being, therefore, KI_3.

We can calculate extinction coefficients for the compound KI_3, substituting m, n and experimental spectrographic data as below in the equations (1′), (3) and (3′).

$m = 1$ $\varepsilon_1^B = 0.22 \times 10^4$ extinction coeff. of iodine at 28×10^3

$n = 1$ $\varepsilon_2^B = 0.32 \times 10^4$,, ,, ,, at 34.5×10^3

The extinction coefficients of the potassium triiodide at wave numbers 28×10^3 and 34.5×10^3 were found to be 1.20×10^4 and 1.58×10^4 respectively.

Substituting these values in the equations (3) and (3′),

i.e., $x = \dfrac{p}{15800-3200}$ and $x = \dfrac{q}{12000-2200}$,

concentrations of potassium triiodide in each case in Fig. 2 and Fig. 3 were calculated. These values of x are shown in Table 4 together with the equilibrium constant calculated for them.

Table 4.

Curve	a (10^{-5}mol/l.)	b (10^{-5}mol/l.)	E_1	E_2	p	q	$\frac{p}{12600}$	$\frac{q}{9800}$	x (10^{-5}mol/l.)	K (10^3)
I	5.0	10 8	0.40	0.57	0.22	0.16	1.8	1.6	1.7	5.7
II	10.0	10.8	0.49	0.67	0.32	0.25	2.6	2.7	2.7	4.6
III	15.0	10.8	0.64	0.89	0.54	0.40	4.3	4.1	4.2	5.9
IV	20.0	10.8	0.75	1.02	0.67	0.51	5.3	5.2	5.3	6.5
V	25.0	10·8	0.79	1.08	0.73	0.55	5.7	5.6	5.7	5.8
VI	30.0	10.8	0.85	1.13	0.78	0.61	6.3	6.2	6.3	5.6
VII	22.5	7.5	0.54	0.74	0.50	0.37	4.0	3.8	3.9	5.8
VIII	20.0	10.0	0.66	0.90	0.58	0.44	4.6	4.5	4.6	5.5
IX	18.0	12.0	0.77	1.04	0.63	0.50	5.0	5.1	5.1	5.7
X	15.0	15.0	0.84	1.14	0.65	0.52	5.1	5.3	5.2	5.4
XI	12.0	18.0	0.90	1.23	0.63	0.50	5.0	5.0	5.0	5.5
XII	10.0	20.0	0.90	1.23	0.57	0.45	4.5	4.5	4.5	5.3
XIII	7.5	22.5	0.91	1.25	0.52	0.41	4.1	4.3	4.3	6.7

The mean value of the equilibrium constant between 23° to 25° is 5.6×10^3. The deviation in the equilibrium constant is supposed to be caused by the flactuation of temperature, as the experiment was carried out at room temperature.

Subtracting the calculated absorption of iodine and potassium iodide from the curve VI which has the mean value of K, the absorption for potassium triiodide is worked out. (Fig. 5)

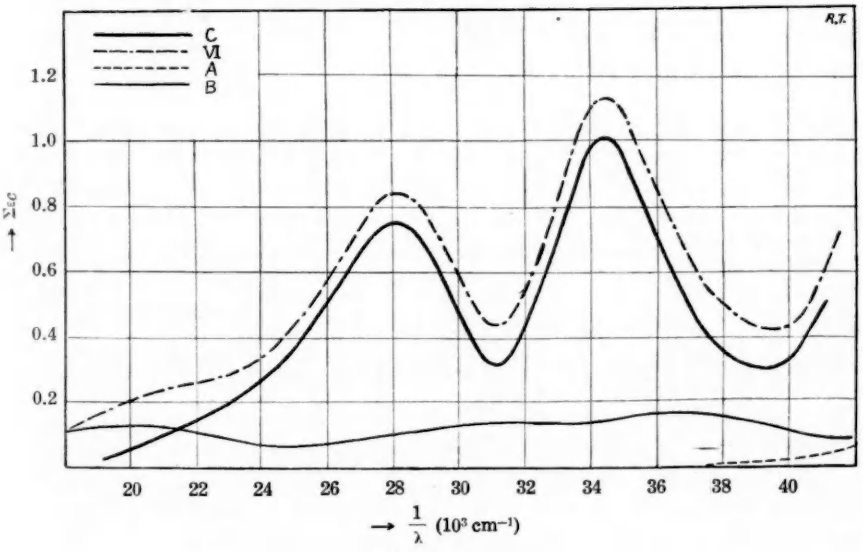

Fig. 5.

The absorption has two maxima at 360 mμ and 290 mμ and minima at 320 mμ and 250 mμ. The extinction coefficients at the maxima are 1.20×10^4 and 1.58×10^4.

An experimental evidence for the relation (6) is given in Fig. 6 in which E_2'' in Table 3 is plotted against x in Table 4.

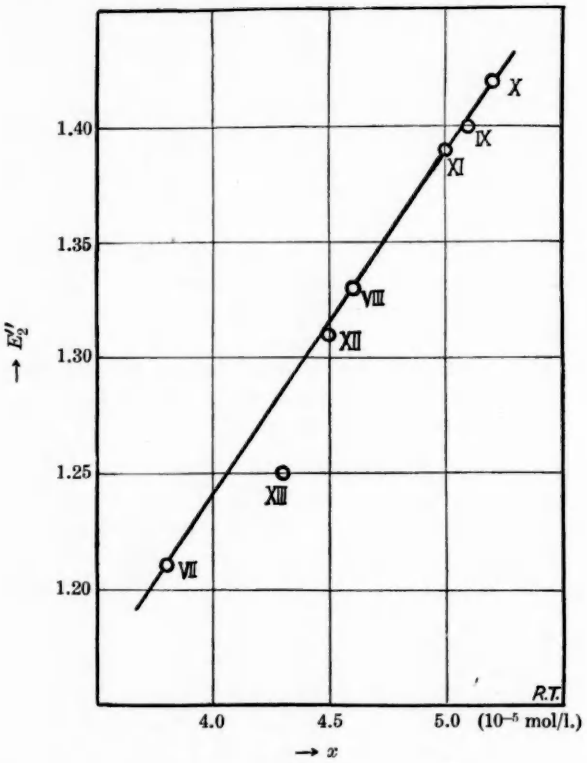

Fig. 6.

Fig. 6 shows that E_2'' is a linear function of x, i.e., the difference of E_2'' is proportional to the difference of concentrations of the compound. The tangent of this line is 15×10^3, and the calculated value of $\frac{\varepsilon_1^B \varepsilon_2^C - \varepsilon_1^C \varepsilon_2^B}{\varepsilon_1^B}$ is 14.8×10^3. ($\frac{\varepsilon_2^B}{\varepsilon_1^B} = 1.1$ from Fig. 2, $\varepsilon_2^C = 15.8 \times 10^3$ as given above and $\varepsilon_1^C = \frac{0.06}{6.3 \times 10^{-5}} = 0.95 \times 10^3$ from Fig. 5 and Table 4.)

As it is clear from the calculation, the relation (6) holds not only for absorption, but also for other physical properties, such as refraction, optical rotation, etc. We may, therefore, take various combinations of physical properties, e.g., absorption at λ_1 and optical rotation at λ_2. This method can be applied not only to the study of molecular compounds as in this example but also can be widely applied to general study of chemical reactions in liquid and in gaseous state.

The examples for these applications will follow.

The author wishes to express his thanks to Prof. Y. Shibata and Mr. C. F. Goodeve for their kind interest in this work.

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THE ISOTOPIC FRACTIONATION OF WATER BY DISTILLATION.

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In the course of purifying water by distillation, we found always some small difference in density between the first and last portions of the distillate. In order to ascertain whether this difference in density is due to the isotopic fractionation of water or to some impurities dissolved therein, we carried out a fractional distillation of a considerable amount of water and measured the densities of its most and least volatile fractions respectively.

The method employed was as follows: The distilling flask was made of glass and fitted with a glass still of Hempel type, 3.5 cm. wide and 17 cm. long, which was filled with glass beads having 4 to 5 mm. diameter up to 6 to 7 cm. height. During the distillation a continuous flow of air free from carbon dioxide was sent through the still column. The distillation was carried out in three stages; namely, in the first stage, a given volume of water was equally divided into the distillate (D_1) and the residue (R_1); in the second stage, both the distillate (D_1) and the residue (R_1) from the first stage were again equally divided by distillation into

the distillate and the residue respectively. We may designate the distillate obtained by the second distillation from the first distillate (D_1) D_2 and at the same time the residue obtained by distilling the residue (R_1) in the first stage may be designated R_2; then in the third stage, both D_2 and R_2 were again divided equally by distillation into the distillate and the residue respectively and the distillate (D_3) obtained from D_2 and the residue (R_3) remained after distilling R_2 were saved for the comparison of their respective densities.

The two fractions thus obtained were at first carefully purified in the same way as described in the preceding paper,[1] the purity being checked by measuring the electrolytic conductivity. Then their densities were compared with that of normal water by a sensitive quartz bouyancy balance. The most volatile part (D_3) which was the last portion of the distillate saved was found to be lighter than ordinary water by 2.5 parts per million (p.p.m.) and the residue (R_3) saved for the density measurement showed an increase in density by 3.8 p.p.m. The difference between these two parts was 6.3 p.p.m. which might be due to the isotopic fractionation of water, if no impurity was occluded during the process of the purification.

Hall and Jones[2] called attention to the fact that a considerable isotopic fractionation occurred during the distillation of highly enriched heavy water under the atmospheric pressure. Our result shows that it is also important to take into consideration the above fact even in the distillation of ordinary water under the atmospheric pressure.

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(2) N. F. Hall and T. O. Jones, *J. Am. Chem. Soc.*, **56** (1934), 749.

THE ISOTOPIC FRACTIONATION OF WATER DUE TO EVAPORATION AND DISTILLATION.

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It has been shown by several investigators[1] that the isotopic fractionation of water occurs either by a slow evaporation or by a distillation especially under a reduced pressure. From this point of view we have examined two samples of water. The first sample was prepared from the mother liquor of the salt which was separated from sea-water by its slow evaporation being exposed to wind and sun. The mother liquor of the salt thus prepared is a brown syrup liquid and contains above all a considerable amount of magnesium chloride in solution which contributes to its bitter taste. Hence it is called "Nigari" (nigai = bitter) in Japanese. The sample water was prepared by distilling the "Nigari" to dryness. The second sample of water was obtained, according to the suggestion of Professor Ikeda, from the molasses of the cane sugar which was prepared by a vacuum distillation of the sap-juice of sugar canes. The molasses was burned in a flow of air and the water formed was twice passed over heated copper oxide for the purification.

The density of the both samples of water, after being carefully purified in the same way as before,[2] was compared with that of the ordinary water by the use of a quartz bouyancy balance. The water from "Nigari" was found, as a result of two determinations, to be heavier than the normal water by 5.4 parts per million. And the increase in density of the water from the cane sugar molasses was found, as a mean of three independent determinations, to be 2.8 parts per million. The increase in the density should be mainly due to the evaporation in the former case and to the distillation in the latter. However, it seems possible that very hygroscopic substances such as magnesium chloride dissolved in

(1) E. W. Washburn, E. R. Smith, and M. Frandsen, *J. Chem. Phys.*, **1** (1933), 288; *Bur. Standards J. Research*, **11** (1933), 453; E. W. Washburn and E. R. Smith, *J. Chem. Phys.*, **1** (1933), 426; *Bur. Standards J. Research*, **12** (1934), 305; *Science*, **79** (1934), 188; G. N. Lewis and R. E. Cornish, *J. Am. Chem. Soc.*, **55** (1933), 2616; G. N. Lewis and R. T. Macdonald, *J. Am. Chem. Soc.*, **55** (1933), 3502; E. S. Gilfillan, Jr., *J. Am. Chem. Soc.*, **56** (1934), 406; R. J. Clark and F. L. Warren, *Nature*, **134** (1934), 29; T. Tucholski, *Nature*, **134** (1934), 29, Cf. also the preceding article.

(2) M. Harada and T. Titani, this Bulletin, **9** (1934), 457.